

THE BONDING OF BIOGLASS TO A COBALT-CHROMIUM
MEDICAL AND DENTAL ALLOY

BY

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The use of Bioglass as a coating on a cobalt-chromium surgical implant alloy gives a composite material which has both the good mechanical properties of the metal and the ability of the glass to form a chemical bond with bone. Good adherence of the glass coating is essential to assure the proper functioning and integrity of the loaded glass-metal implant in vivo.

A shear strength test was developed so that the effect of various factors (such as surface roughness) on glass-metal bond strength could be determined quantitatively. Test results showed that adherence between glass and metal is more dependent on chemical bonding than on mechanical interlocking.

Analyses of the glass-metal interface by Auger electron spectroscopy (AES), electron microprobe (EMP), and scanning electron microscopy (SEM) were used to determine the compositional profiles and surface characteristics which are associated with high bond strength. The thickness of the oxide layer formed on the alloy prior to the coating operation is the key factor which determines the strength of the bond formed between glass and metal. For test specimens with high bond strength, fracture typically occurs between the metal and metal oxide layer. Specimens with low bond strength either fracture a) within the oxide layer if this layer is too thick or b) between the glass and metal if no oxide layer is present. Prolonged heating of a coated specimen with good bond strength decreases glass-metal adherence due to loss of metal oxide saturation in the glass or the formation of voids at the interface.

Fatigue strength of the glass-metal bond was found to be lower for coated specimens tested in vivo, with the observed loss of strength attributed in part to the presence of porosity at the interface. In vivo tests using Bioglass-Vitallium implants showed that 1) bond strength of the coating under various types of loading is more than adequate, 2) the reactivity of the Bioglass is not affected by the immersion coating operation, and 3) there is no incidence of increased corrosion at the glass-metal junction due to metal sensitization.

CHAPTER I INTRODUCTION

Metals, Ceramics, and Glass as Implant Materials

The use of metal and ceramic materials in the human body has become increasingly widespread in the past twenty years. Metals are commonly used in medical devices such as hip and knee prostheses, heart valves, and electrodes; and in dentistry as crowns, implants, and filling materials. Ceramics are used both as permanent structural implants, such as high density alumina for femur replacements, and as temporary support implants which soon dissolve in the body (e.g., calcium phosphate). The use of glass in the body has been traditionally restricted to applications which require proper esthetics--such as the porcelain used to simulate tooth enamel.

At the present time the primary use of glass-metal composite devices or restorations in the human body is the porcelain-fused-to-metal crown used in dentistry. This type of restoration is widely used for anterior teeth because of the desirable combination of the strength of the metal and the natural, toothlike appearance provided by the enamel (glass).

A requirement of all implant materials is that they are tolerated by the body after implantation. Any adverse reaction in response to the implant, such as inflammation or increased incidence of infection, can lead to its failure and removal. Even with a relatively well-tolerated,

inert material such as alumina, the body typically responds by isolating the implant from the rest of the system by surrounding it with a fibrous capsule.

Many of the problems associated with the use of biomaterials are caused by the methods of fastening the implants in their proper position. Structural or load-bearing devices are usually fastened in place by cements such as polymethylmethacrylate (e.g., for hip prostheses) and zinc phosphate (e.g., for metal crowns), or by mechanical means such as screws and fasteners on a metal splint, or by press-fitting the specially shaped implant into a prepared space in the bone. Often these methods of attachment cause bone resorption around the implant leading to loosening and possibly fracture and thus necessitating the removal of the device. Other undesirable effects which can lead to subsequent removal of the implant are the exothermic reaction and monomer release to the system resulting from the use of PMMA cement, and the wear particles and corrosion products in the tissues from metallic devices and fasteners.

Porous materials which allow tissue ingrowth to provide mechanical fixation of the implant in its proper position have been developed in order to overcome the problems associated with other methods of fixation. Tissue ingrowth and partial fixation have been observed with both metallic and ceramic porous materials, but these materials have been generally unsatisfactory for use as load-bearing implants because their increased surface area leads to more corrosion and dissolution, and their porous structure results in an implant with much lower mechanical properties (especially fatigue strength) as compared to the dense materials.

The Development of Bioglass

The use of both porous material and the conventional methods of mechanical fixation of the implant to bone has been observed to be unsatisfactory in many cases. This has led to the development of a new class of bioactive material which forms a direct chemical bond with bone. A series of glasses and glass-ceramics whose compositions fall within a specific range has been developed by L. L. Hench and others and given the name "Bioglass."¹⁻⁴ These glasses contain primarily CaO , P_2O_5 , Na_2O , and SiO_2 , with some limited substitution of other oxides such as CaF_2 and B_2O_3 possible in order to modify the reactivity or fluidity of the glass, if necessary. The composition and reactivity of Bioglass are such that the body makes no attempt to isolate it from the rest of the system by the formation of a fibrous capsule.

The mechanism by which Bioglass forms a strong bond with bone has been extensively studied and is well documented.^{5,6} Initially, Na^+ , Ca^{2+} , and P^{5+} ions leach out of the glass leaving a silica gel structure, the thickness of which depends on such factors as time of exposure of glass to the solution. As osteoblasts begin to lay down new bone substance around the implant, the Ca and P leached from the Bioglass preprecipitate out of the solution and form an amorphous layer on the silica gel matrix. Thus a graded interface is formed consisting of Ca and P from the Bioglass and the Ca and P (hydroxyapatite) of the new bone, and a chemical union between the Bioglass and the bone is established. Microscopic examination of this interface shows highly elongated hydroxyapatite crystals bridging the space between the gel layer of the implant surface and mature bone.

The bond between bone and Bioglass typically exhibits a strength of 75% of that of dense cortical bone, and the bond area itself is often stronger than the surrounding bone if sufficient time is allowed for full development of the bond (generally around 6 weeks).⁷ Factors such as vibration or movement of the implant⁸ or the presence of undesirable elements such as alumina⁹ at the bone-Bioglass interface during early stages of bond formation can be detrimental to bone formation and little or no bonding will occur.

Bioglass-Coated Implants

The ability of Bioglass to form a direct chemical bond to bone with only a small surface zone (usually about 100 μm thick) being affected by leaching means that the original strength of the bulk material is retained. Unfortunately, Bioglass, like most glasses, is relatively weak in tension and is subject to crack formation, propagation, and brittle failure. Therefore, its use as a bulk material for load-bearing applications in orthopaedics or dentistry is doubtful. The ideal use of Bioglass in load-bearing applications is as a coating on a stronger material such as stainless steel or high density alumina. The thin Bioglass coating reacts to bond the implant to bone, while the substrate metal or ceramic provides the strength necessary to withstand the normal forces to which the implant is subjected. This necessitates the formation of a good bond between the Bioglass and the substrate so that the forces are transmitted from the weaker outer layer of glass to the bulk of the implant.

There are a number of factors to be considered when selecting an implant material to be coated with Bioglass:

1. The material must have high strength to withstand the complex tensile, compressive, and torsional loads it will be subjected to as an implant.
2. It must have a high modulus of elasticity, as excessive bending under load will cause fracture of the glass coating.
3. It must have been previously certified as an acceptable implant material, both to facilitate the acceptance of the coated device with the medical profession and to avoid the long times necessary to certify a new material for use in the human body.
4. It ideally should have a thermal expansion coefficient similar to Bioglass because of the necessity of heating and cooling the coated device during the coating operation.

High density alumina is a high strength, high modulus material which shows promise for use in both orthopaedics and dentistry. There are several drawbacks to the use of alumina, however, one of which is its observed loss of strength in a physiological environment. Fatigue tests on 65% dense alumina in simulated body solutions showed a reduction in strength of an average of 35% after 12 weeks,¹⁰ and other tests have shown that there is also reason for concern about the loss of strength of high-density alumina in various solutions.¹¹

A limitation of the use of alumina as a substrate for coating with Bioglass is the large difference in its thermal expansion coefficient (about $8 \times 10^{-6}/^{\circ}\text{C}$) as compared to that of Bioglass ($13\text{--}15 \times 10^{-6}/^{\circ}\text{C}$). Not only is there an excessively large stress level produced at the interface during cooling from the coating temperature, but also the lower expansion of the substrate puts the glass layer in tension, thus enhancing its tendency to crack.

To overcome this alumina-Bioglass expansion mismatch and avoid possible failure of the coated device, Greenspan¹² developed a method of double coating the alumina substrate. In this method the inner layer of Bioglass takes up the expansion mismatch so that the second layer has little strain imposed on it during cooling and an expansion-graded interface is established which, while not ideal, appears to be satisfactory. After a series of successful tests of the Bioglass-coated alumina system as dental implants in primates,¹³ clinical trials are now being designed for humans. However, development of successful Bioglass-coated alumina orthopaedic devices appears many years away.

There are several advantages to using metals such as stainless steel or cobalt-chromium alloys rather than alumina for Bioglass-coated implants. Metals have long been used in load-bearing applications in the body, have good fatigue strength in a physiological environment, and are not as subject to brittle failure as ceramics. Also, the higher thermal expansion of these metals ($13-16 \times 10^{-6}/^{\circ}\text{C}$) is very similar to that of Bioglass.

The Development of Bioglass-Coated Metal Implants

The coating of metals has long been a part of the Bioglass development program. Some of the original work was performed at the University of Florida using 45S5 Bioglass for coating a stainless steel substrate. An enameling method was used in which the glass was placed on the metal as a frit, and the substrate taken to a temperature where the frit particles fused and formed a uniform glass coating. This method was

unsuccessful because metal ions diffused from the substrate through the glass to the surface.

A second direction was taken which involved the use of a commercial ground coat (Ferro and Pemco Corporations) applied first to the stainless steel substrate with Bioglass applied as a second coating. However, metal ion migration was again a problem as the transition metals in the ground coat and Fe and Cr from the steel were found on the Bioglass surface after heating to the high temperatures necessary to fuse the frit particles and to form a smooth, glossy surface. The concentration of the metal ions on the Bioglass surface was sufficient to render the coating unsatisfactory for biological applications.¹⁴

A third approach was taken a few years later by the Leitz group in Germany, using a surface active glass similar in composition to Bioglass, but termed Ceravital.¹⁵ They applied and fired a ground coat to stainless steel using standard enameling techniques, then fused crystallized glass-ceramic Ceravital granules to the ground coat in a separate process. This two-step procedure caused the formation of a rough granular surface but limited the migration of Fe and Cr. Unfortunately, recent results have shown that there is a continuous biological attack of the glass-ceramic granules and breakdown of the interfacial structure in contact with bone.

A flame-spray coating method was developed at the University of Florida in an attempt to get a uniform coating of Bioglass without having to heat the metal substrate to the glass softening temperature.¹⁶ This method was partially unsuccessful because of the porosity which

developed at the glass-metal interface as the hot glass particles struck and fused to the metal surface. Another problem with flame spraying Bioglass was the high viscosity of the glass at the coating temperature. Lower-viscosity Bioglasses containing fluorine and boron were developed which enabled the production of smooth, uniform glass coating on the steel substrates.¹⁷ However, porosity at the interface was still a problem and in vitro tests showed the coating to have low fatigue strength as well as excessive corrosion at the glass-metal interface.¹⁸ Also, a number of flame-spray-coated hip implants failed after in vivo testing in monkeys.

In an attempt to overcome some of the problems inherent in the flame spray coating method, Buscemi and Hench developed an immersion process for coating Bioglass to metal.¹⁹ In this technique the metal substrate is immersed in molten Bioglass for short times (e.g., 3 sec) and then withdrawn at a rate which allows the excess glass to flow off leaving a fairly uniform coating of the desired thickness. Porosity is typically observed at the glass-metal interface of immersion coated specimens, but not to the extent seen in flame-sprayed specimens.

The bond strength of immersion-coated specimens appeared to be higher than flame coated ones as judged by observing the integrity of the coating after quenching the coated specimens in water from various temperatures. In vivo tests showed immersion coated 316L stainless steel implants withstood tensile loads of 60 and 137 lbs after 8 weeks implantation time without failure of either the glass-metal or glass-bone interfaces.²⁰ However, quench test results on immersion coated

Vitallium* indicated that Bioglass formed a better bond with this surgical grade Co-Cr alloy than with 316L stainless steel. In addition, the corrosion susceptibility and interfacial bond strength of Bioglass-coated Vitallium chips implanted in rats were superior to similarly coated stainless steel implants from previous tests.²¹

After evaluating the results of all the tests of bond integrity as well as the preliminary in vitro and in vivo testing, it was determined that Vitallium was the metal of choice for use as a substrate for coating with Bioglass.

Characteristics of Vitallium

Vitallium is an alloy of cobalt, chromium, and molybdenum which falls into the general classification of a super alloy. Some industrial alloys of this group, such as Haynes Stellite-21, are very similar to Vitallium in composition. These alloys have been developed primarily for applications which require metals with high creep-rupture strength and corrosion resistance at temperatures over 800°C. Typical applications are as either forging or castings for turbine discs and blades, nozzle vanes in jet engines, and in sheet metal assemblies such as combustion chamber lines, tail pipes, and after burners.²² Molybdenum is added to these alloys as a solid solution strengthener at room temperature, and imparts much better creep resistance at higher temperatures. Chromium gives these alloys their excellent corrosion resistance.

*Howmedica, Inc., Chicago, Illinois

Vitallium and similar Co-Cr alloys were first developed for removable partial denture castings in about 1930, and by 1950 over 80% of all partial dentures were made from these alloys.²³ Because of its excellent corrosion resistance and relative inertness in the body, Vitallium has found wide use as a surgical implant alloy for such applications as total hip replacement and dental implants.

A wrought form of Vitallium (FHS) has recently been developed to give increased strength to the alloy for applications in which a load-bearing implant is required. Table 1 gives a comparison of the composition and properties of both the wrought and standard cast Vitallium alloys.

Objectives of This Research

The primary objective of this research is to determine the nature of the bond formed between Bioglass and Vitallium using suitable analytical techniques and to correlate the findings and observations of this study to the prevailing theories on glass-metal bonding. Some of the secondary objectives of the overall research program are:

1. Optimize the immersion coating process to obtain a Bioglass-Vitallium bond of maximum strength, and thus increase the reliability of the composite implant device for use in animal and human tests.
2. Develop a suitable testing method to monitor progress in increasing bond strength and to give a quantitative shear stress measurement which can be used to predict the reliability of a glass-metal composite in actual service conditions in the body.
3. Determine if the coating process alters the reactivity or bone-bonding ability of the Bioglass.

Table 1
Chemical Analyses of Cast and Wrought Vitallium Alloys

Alloys	C	Si	Mn	Cr	Mo	Co
Cast Vitallium [®] Alloy	.25	.75	.70	28.0	5.5	balance
FHS [®] Vitallium [®] Alloy	.05	.75	.70	26.5	5.5	balance

[®]Howmedica, Inc.

Table 2
Bioglass® Compositions

Nomenclature: $\frac{52\text{ S}}{4.6}$ 52% Si Ca/P Mole Ratio	
<u>52S4.6 Bioglass</u>	
<u>Oxide</u>	<u>Wt %</u>
SiO ₂	52
CaO	21
Na ₂ O	21
P ₂ O ₅	6
<u>45S5F Bioglass</u>	
<u>Oxide</u>	<u>Wt %</u>
SiO ₂	45
CaO	12.25
CaF ₂	12.25
Na ₂ O	24.5
P ₂ O ₅	6

4. Establish the susceptibility of the glass-metal interface to corrosion and fatigue.
5. Determine the microstructural and surface compositional factors responsible for good interfacial bonding.
6. Attempt to resolve some of the controversy in the literature about the exact nature of glass-metal bonding and the relative importance of chemical and mechanical factors on bond strength.

CHAPTER II GLASS-METAL BONDING

Glass-Metal Devices and Applications

Devices which include glass-bonded-to-metal composites are used in a wide variety of applications. For example, there are a number of electronic devices in which proper glass-metal sealing is an important part in the ability of the component to function properly. One common application is the sealing of metal wires to glass envelopes in forming connections such as in light bulbs or electron tubes. Also, glass frit in a silver conductive paint is used to form the seal (when fused) between metal lead wires and ceramic capacitor bodies.

Porcelain-enameled steel is another commercial product in which good glass-metal bonding is essential. Enameled steel or iron is used for such household items as refrigerator and stove side panels, cooking pans, and bathtubs. The porcelain coating is added to enhance the abrasion and corrosion resistance of the steel, as well as to improve its appearance. The porcelain coating (usually about 0.5 mm in thickness) typically consists of a blue ground coat and outer coat of white or colored opaque material.

The porcelain-fused-to-metal crown used extensively in the restoration of anterior teeth also depends on a good glass-metal bond for proper functioning. A thin metal casting (either of gold alloy or a non-noble

alloy such as nickel-chromium) fits over the preparation of the remaining tooth structure and provides strength to the restoration. The natural tooth-like appearance of the composite restoration is provided by the translucent porcelain. In preparing the glass-metal crown, a layer of opaque porcelain is put on as a frit then fired so that a thin, opaque coating is formed which masks the color and reflectivity of the metal. One or more layers of properly colored porcelain frit are then added and fired so that the finished restoration has the translucency and color of the surrounding natural teeth.

Methods of Coating

There are basically four methods of coating a metal substrate with glass:

1. Application of the glass in particle or frit form, then firing to form a uniform coating.
2. Flame spray coating of glass particles on the metal substrate.
3. Immersion of the metal substrate into molten glass.
4. Sputter coating a thin layer of glass onto the metal substrate in a vacuum.

Of these methods, fusion of fritted glass on the metal surface is by far the most commonly used. Commercial enameling is accomplished by first dipping or spraying the metal piece with porcelain frit suspended in a liquid solution, then firing the frit-coated metal until a homogeneous glass layer is formed. A blue ground coat containing cobalt and nickel oxides is often put on the metal first to promote better adherence between the final decorative coat and the metal substrate.

Glass-to-metal sealing of electronic components is also accomplished by fusing low-melting glass frit to the metal and glass surfaces to be joined. Important considerations are that the glass should wet the metal and the two should have similar thermal expansion coefficients since the whole device must be heated to allow melting of the glass frit.

In the fabrication of a dental crown, the porcelain is also put on the metal substrate as a frit and the entire restoration fired to a suitable temperature (usually in a partial vacuum). In this firing operation, as in all cases in which the glass is put on the substrate as a frit, it is imperative that the metal has a substantially higher softening temperature than the glass so that creep and deformation of the metal substrate do not occur.

Flame spray coating is a technique more often used for the coating of higher-melting glasses and refractory oxide ceramics onto metal substrates. An example is the alumina coating applied by flame spraying to a titanium alloy for orthopaedic implant applications. The principal advantage of this technique is that the metal substrate does not have to be taken to a high temperature to allow fusion of the glass or ceramic particles. The coating particles are fused while passing through a suitable flame (such as that of an oxy-hydrogen torch) before striking the preheated metal substrates. This combination of heat and impact causes the glass to flow and form a homogeneous coat at lower temperatures than are possible using the conventional method of fritting and then firing the coated metal substrate.

Immersion of the metal substrate into molten glass is a third technique for coating metal with glass. This method is rarely used in commercial product coating because it is expensive and does not lend itself well to a production line operation. Coatings by this method tend to be somewhat thicker than with other techniques, and the coating of complex shapes is more difficult. An advantage of using this technique is that the metal substrate can be preheated to a low temperature and the time of contact with the molten glass can be kept short so that the metal undergoes little change in microstructure or mechanical properties.

A fourth coating method is the sputtering of a glass onto a metal substrate in a vacuum. By properly locating a glass piece in the path of charged ions in a bell jar, the rapidly moving ions knock off small pieces of the glass sending them in all directions within the chamber. If a metal substrate is placed in the path of the heated glass molecules, a coating on the metal surface is slowly built up with time. Precision coatings can be applied by this method, but it is the most expensive of the four coating techniques on a cost-per-piece basis. Only thin coatings are usually produced by this method because the rate of deposition of glass is so low that it is difficult to get a thick coating in a reasonable time. For example, a new technique of ion beam coating (using argon ions) produces a glass coating at a rate of only 5000 Å per hour.

Nature of Wetting

Whatever the method used for applying a glass coating to a metal, the molten glass must first wet the surface of the metal in order for the coating to form a bond with the substrate. The degree of wetting can be estimated by measuring the contact angle that a drop of molten glass makes on the surface of the metal substrate. This angle can be measured by use of a goniometer²⁴ or calculated by the relation:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$

where θ is the contact angle and γ_{LV} , γ_{SV} , and γ_{SL} are the interfacial energies between the liquid-vapor, solid-vapor, and solid-liquid phases, respectively. A θ of less than 90° is generally indicative of good wetting, whereas larger contact angles indicate the absence of wetting.²⁴ Simply having an acute contact angle is not enough to guarantee good wetting however, as θ must approach 0° to get spreading or proper wetting on some surfaces.

One problem in the bonding of glass to metal or vice versa is that the surface energies of the two materials are greatly different in value. For example, surface energies for most silicate types of glasses range from about 250 to 400 ergs/cm². The surface energies of metals are higher, ranging from about 1000 to 1800 ergs/cm².²⁵ This difference leads to poor wetting, which may be desirable in certain cases such as non-wetting of a refractory ceramic furnace liner by molten metal. In attempting to bond glass to metal, however, it is absolutely essential that the molten glass wet the metal substrate. If a condition of poor

wetting exists, the glass will not penetrate into the valleys of the surface roughness (on a microscopic scale). If this condition exists, only the peaks will be contact points and only a fracture of the existing metal surface area is available for chemical bonding or mechanical interlocking.

There are essentially two ways of overcoming the surface energy differences of glass and metal so that good bonding can occur. The first is by saturating the glass with the oxide of the substrate metal. King, Tripp, and Duckworth²⁶ found that porcelain frit applied to an iron substrate and fired in an argon atmosphere produced little or no wetting of the iron by the enamel. However, if the saturation limit of 43% FeO was added to the porcelain composition, excellent wetting (and bonding) of the iron was observed under identical conditions. As the iron oxide content of the porcelain was reduced to 40% FeO, the wetting became poor and no adherence of the porcelain to metal was observed. The impracticability of adding the saturation limit of metal oxide to every glass to be enameled to metal is obvious and would not be possible in cases where the glass compositions are rigidly established.

Fortunately, the other means of producing better wetting between molten glass and metal is much easier to accomplish and is ideal for most situations. It involves simply oxidizing the metal substrate so that the molten glass comes in contact with an oxide rather than a metallic surface. As the similar structure of glass and metal oxide gives rise to similar surface energies, good wetting of the glass on metal usually occurs. Excellent glass-to-metal bonding is now possible if other conditions have been properly controlled.

Theories of Adherence

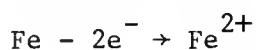
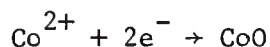
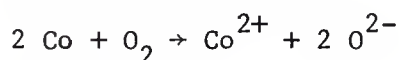
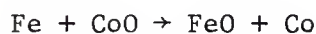
There have been numerous studies in past years on glass metal bonding, but there is still a lack of agreement among researchers as to the exact nature of the bond formed when a glass coating is applied to a metal substrate. For example, some studies have shown that adherence is caused by reactions which are chemical in nature, while other investigations have demonstrated that adherence is primarily a function of mechanical factors such as glass-metal interlocking. Much of the published work on glass-metal bonding has been concerned with understanding and improving the enameling of glass coatings on steel.^{27,28} Other prominent areas of investigation are the bonding of dental porcelain to metals (especially gold),²⁹⁻³¹ and the improvement of glass-metal seals for electronic devices.³²

Many of the older studies (e.g., 1930-1950) on glass-metal bonding tended to emphasize the importance of the mechanical interlocking of the glass to the metal surface as the principal cause of adherence. In porcelain enameling of steel, for example, major emphasis was placed on the proper roughening of the metal surface prior to the application of the glass frit. A comprehensive investigation by the National Bureau of Standards in 1953 was in agreement with earlier studies which concluded that mechanical factors best explained the observed glass-metal adherence.³³ In that study the character of the interfacial roughness and the measured adherence between glass and metal was correlated with both the density of the anchor points of the glass at the metal surface and the specific surface area of the metal. Their conclusion that

adherence is primarily mechanical in nature was based upon results which showed that specific surface area (or the area available for chemical bonding) is much less important than the increased mechanical interlocking provided by a higher anchor point density.

The surface roughness of a metal can be increased by such techniques as grit blasting, or it can be produced on a microscopic scale by the phenomenon of electrogalvanic corrosion. The increase of surface roughness in the porcelain enameling of steel by electrogalvanic corrosion has been observed by a number of investigators.^{34,35}

Roughening of the metal surface has been observed when the porcelain ground coat contains NiO or CoO. The metals of these oxides precipitate from the glass layer next to the steel forming a short circuited local cell with iron as the anode. The equations for a typical reaction involving CoO can be written as³⁴



The current flows from the iron to the cobalt at the interface and back to the iron completing the circuit. Once these cells are established they continue during firing in air because there is sufficient oxygen and anodic iron available. This reaction causes iron to go continually into solution in the glass (as Fe^{2+}) with a corresponding roughness of the surface and anchoring of the glass into the newly formed holes.

The same mechanism which is responsible for electrogalvanic corrosion can also cause the precipitation of metal dendrites in the glass. These dendrites can occur as isolated specks in the glass or they can extend into the glass while connected to the metal surface.³⁶ In the latter case, they can act as anchors since they project into the glass phases. However, the effect that these dendrites have on glass-metal bonding has not been established, and some researchers feel that they do little to increase adherence.²⁶ On the negative side, in some cases the presence of a precipitated metal at the interface could act as a parting layer between the glass substrate, thus causing a loss of adherence.

In recent years an increasing number of investigators have concluded that chemical bonding is the primary cause of adherence between glass and metal. Good adherence is caused by chemical bonds (i.e., ionic, covalent, or metallic) which are established at the glass-metal interface rather than the much weaker Van der Waals bonds. One way to characterize the nature of chemical bonding is to represent it as the presence of a continuous electronic structure across the glass-metal interface. To have metallic bonding and a continuous electronic structure, metal ions must be present in the glass, oxide layer, and metal substrate.

There are several ways of establishing a condition of chemical bonding between glass and metal assuming good wetting of the substrate has occurred. One necessary requirement is that the interfacial area be in equilibrium. For equilibrium to be present, one condition is

that the glass interfacial layer must be saturated with the lowest valent oxide of the metal substrate. For example, in the porcelain-steel system this would mean that FeO should be present rather than Fe_2O_3 .

Another way of establishing the condition of equilibrium at the interface is to have at least a monolayer of oxide between the metal and glass. This is the ideal situation to have if the temperature cycle and other processing conditions can be controlled so that the molten glass just dissolves the oxide down to the last molecular layer. In porcelain enameling of steel, however, it is very difficult to terminate the firing cycle so that a monolayer of oxide is left between glass and metal. Too little time at temperature leaves a thick oxide layer (and bonding is usually weak between iron and its oxide), while too much time results in the entire oxide layer being dissolved in the glass.

Borom and Pask³⁷ found that if a glass-metal interface is held at a high temperature after the oxide layer has completely dissolved, diffusion of the metal oxide away from the interface occurs. Thus the equilibrium condition at the interface is destroyed because there is no longer a saturation of the metal oxide in the layer of glass next to the metal surface. The effects of this loss of saturation are in agreement with the study of King et al.²⁶ which found that all adherence between glass and metal was lost if the percentage of FeO in sodium disilicate glass was reduced from 43% to 40%. Hoge et al.³⁸ also found that maximum adherence occurs when the glass at the interface

is saturated with the oxide of the lowest valent cation of the substrate metal. It appears that saturation of the metal oxide is necessary only in the glass layer next to the metal substrate, and if this condition is altered by diffusion of the metal ion (or oxide) away from the interface then bonding strength decreases.

The measurement of contact angles of glass on metal in some studies has demonstrated the importance of maintaining saturation of the metal oxide. Cline et al.³⁹ observed that the contact angle of sodium silicate glass on iron decreased from 55° to 20° when an oxide layer was formed (Fe_3O_4), but increased back to 55° when this oxide layer was completely dissolved. Adams and Pask⁴⁰ showed that the glass must be saturated by the oxide of the substrate metal (not just any oxide), as increasing the FeO content in silicate glass to the saturation point did not have any effect on the contact angle or adherence of the glass on a platinum substrate.

The other means of establishing chemical equilibrium at the interface is by setting up proper conditions so that redox reactions occur between the metal substrate and some metal oxide in the glass. This is often necessary in porcelain enameling of steel, since after the glass layer forms no more atmospheric oxygen can get to the interface to oxidize the metal substrate. If heating is continued past the point where the oxide layer is completely dissolved, diffusion of the metal oxide away from the interface leads to a loss of equilibrium and thus a replacement of chemical bonds with Van der Waals bonds.⁴¹ If oxygen can be supplied by the reduction of an oxide in the glass by a suitable

redox reaction, oxidation of the metal substrate can continue without the need of atmospheric oxygen and interfacial saturation can be maintained.

Thus the key to maintaining chemical equilibrium by interfacial saturation is to either stop the dissolution of the substrate oxide layer before it is completely dissolved by the glass, or to have some metal oxides (called adherence oxides) present in the glass which can be reduced to give free oxygen. An example of these adherence oxides is the NiO and CoO present in the ground coat of commercial porcelain enamel.

Bioglass Coating Methods

There are several reasons for the selection of the immersion method as the preferred technique for coating Vitallium with Bioglass. The frit enameling method of obtaining a glass coating is unacceptable because the relatively long time at elevated temperature required to cause softening and flow of the glass frit results in diffusion of metal ions completely through the thin glass coating. Also, one of the objectives of this research is to optimize the coating of the wrought Vitallium FHS alloy as it has potentially more uses as an orthopaedic or structural implant material than does the cast Vitallium alloy. The wrought alloy cannot be heated over 650°C for any significant time if its high mechanical properties are to be retained. The same maximum temperature applies to the cast Vitallium alloy as well, as higher temperatures cause excessive carbide precipitation and a corresponding

loss of ductility in this alloy. This eliminated the frit enameling method of coating either the cast or wrought Vitallium alloys since a temperature in the range of 1000°C is required for Bioglass to soften and flow.

The flame spray coating method has been used with some success in past coating work, but specimens coated by this technique typically show a greater number of voids and bubbles at the Bioglass-metal interface as compared to specimens coated by the immersion method. The sputter coating of glass on metal by ion beam bombardment is a technique which is still in the development stage and requires equipment which is not commonly available. The coating of Bioglass on metal, ceramic, and polymer substrates by this technique is currently taking place at NASA-Lewis Research Center, but a major research effort may be required to optimize the coating variables so that a satisfactory coating is obtained. This method will only be practical for obtaining relatively thin coatings, and the coating of complex shapes containing internal or shielded surfaces is not possible.

Although the immersion method appears to be the most satisfactory coating technique for the Bioglass-Vitallium system, there are a number of reasons for conducting a concurrent study of coating by the frit enameling method. The most valuable information to be gained by such a study is a better understanding of the nature of the glass-metal interface formed. The two coating techniques are quite different in such factors as time of interface at coating temperature, for example, and the direct comparison of the metal-glass interfacial characteristics

and resulting bond strengths observed may aid in understanding the relative importance of such factors. Also, a correlation of the results from the Bioglass-Vitallium system with the much studied porcelain-steel and dental porcelain-metal systems produced by the same coating method can be obtained.

Summary

There are a number of reactions that occur in the porcelain enameling of steel which cause increased adherence of the glass to the metal. Increased surface roughness and thus the potential for more mechanical interlocking is caused by the reduction of certain oxides in the glass which have an oxidation affinity which is lower than that of the substrate metal. From the standpoint of chemical adherence, reducible oxides in the glass are also required so as to maintain the interfacial saturation of the glass with the oxide of the metal substrate.

The standard free energy of formation of metal oxides can be used to determine which oxides in the glass will be reduced when in contact with the metal substrate at a given temperature. Thermodynamic data⁴² for selected oxides at three temperatures are given in Table 3 in order to show the change in oxidation/reduction potential across the glass-metal temperature gradient. The lowest temperature (700°C) is slightly higher than the average preheat temperature of the metal, while the highest (1300°C) is close to the temperature of the molten glass. During immersion the cooler metal substrate is

Table 3
Free Energy of Formation of Metal Oxides

Reaction	Energy (K cal/mole O ₂)		
	700	1000	1300
2 Ca + O ₂ → 2 CaO	-255	-242	-226
4 Li + O ₂ → 2 Li ₂ O	-226	-207	-188
4/3 Al + O ₂ → 2/3 Al ₂ O ₃	-218	-202	-185
Si + O ₂ → SiO ₂	-166	-153	-140
4 Na + O ₂ → 2 Na ₂ O	-134	-105	---
4/3 Cr + O ₂ → 2/3 Cr ₂ O ₃	-138	-125	-112
4/5 P + O ₂ → 2/5 P ₂ O ₅	- 98	- 87	- 70
2 Fe + O ₂ → 2 FeO	- 95	- 87	- 78
2/3 Mo + O ₂ → 2/3 MoO ₃	- 94	- 83	- 69
2 Co + O ₂ → 2 CoO	- 78	- 67	- 56
2 Ni + O ₂ → 2 NiO	- 74	- 60	- 46
2 Cu + O ₂ → 2 CuO	- 39	- 31	- 27
C + O ₂ → CO ₂	- 95	- 95	- 95
2 C + O ₂ → 2 CO	- 94	-107	-119

heated by the molten glass, drawing some heat away from the surrounding layer of glass. An intermediate temperature such as 1000°C may best represent the actual condition at which the given reactions will occur.

Oxides with higher negative free energy of formation are more stable and will not be reduced when in contact with any metal lower on the chart. A metal higher on the chart will reduce a lower oxide to base metal if favorable thermodynamic conditions are present. For example, in the firing of a commercial porcelain ground coat at 870°C, it is obvious from the chart that CoO and NiO will be reduced when in contact with the steel substrate.

For the Bioglass-Vitallium system, however, the glass does not contain any oxide which can be reduced by cobalt (the major element in Vitallium). Cobalt is below calcium, sodium, phosphorous and silicon in its affinity for oxygen so reduction of any of the oxides of these metals is not possible in the range of temperatures present during the coating process. If the metal substrate was pure cobalt, such mechanisms as electrogalvonic corrosion (causing increased surface roughness) would not take place. Vitallium does contain a significant amount of chromium (25-30%), and this metal has the potential for reducing two components in the glass under proper conditions. From Table 3 it can be seen that P_2O_5 is the most likely oxide to be reduced by chromium, with Na_2O being the other possibility. Vitallium also contains a small amount of molybdenum, but its oxidation potential is below that of any component in the glass.

The addition of an oxide such as CuO to the basic Bioglass composition would make available an oxide in the glass which can be reduced by either the cobalt or chromium of the substrate metal. However, modifications in the chemical composition of Bioglass are generally not acceptable because there is only a narrow range of compositions in which bonding of the glass to bone will take place. Even minor chemical modifications would require extensive animal testing to recertify the altered material.

Although the bulk of the experimental work is concerned with optimizing the immersion process for the coating of wrought Vitallium with Bioglass of the standard 52S4.6 composition, it is desirable to include the testing of a modified glass composition by a conventional frit enameling procedure in order to gain more insight into the relative importance of such factors as increased surface roughness on adherence. Some specific questions which can be answered by this approach are:

1. Can interfacial roughening occur by reduction of certain oxides in the standard Bioglass by the chromium in the metal substrate, or does it take an oxide which is below both cobalt and chromium in free energy of oxide formation?
2. Does the long time at temperature of the frit-enameling method cause significantly more interfacial roughening than the immersion method with its short contact time?
3. Does increased interfacial roughness increase the glass-metal bond strength?
4. Do conditions necessary for chemical equilibrium to be established (e.g., a glass layer saturated with metal oxide at the interface of the substrate) vary depending on the coating method?

CHAPTER III EXPERIMENTAL PROCEDURES

Laboratory Procedures, Equipment, and Materials

The Bioglass used for most of the experimental work in this study was a special high purity glass of the composition 52S4.6. An analysis of this glass is given in Table 2. Some of the initial work for this study was accomplished using 52S4.6 glass which contained a higher level of impurities and could readily be distinguished from the purer, colorless glass by its slight greenish color. The purity of the Bioglass had no effect on glass-to-metal bonding, and the only concern with using a slightly impure glass would be the effect of the trace metallic impurities on the formation of the Bioglass-bone bond.

In the initial stages of this research study, several types of crucibles were used in order to determine which type was most suitable for containing molten Bioglass for long periods of time. For test purposes, Bioglass of the 52S4.6 composition was brought to 1350°C simultaneously in alumina, magnesia, zirconia, and fused silica crucibles and held at this temperature for periods of time as long as four days. Upon examination, each of these crucible types showed evidence of having been dissolved to some extent by the Bioglass. The fused silica crucibles were initially chosen as most acceptable because of 1) the relative low dissolution of this type by the glass and 2) the presence of slightly higher

silica in the Bioglass composition should have a minimal effect on bone-Bioglass bonding. Alumina crucibles are the least desirable as even a small amount of alumina in the Bioglass has been shown to be detrimental to its ability to form a chemical bond with bone.⁹ The effects of ZrO_2 and MgO on the bonding of Bioglass to bone are not known at this time. Although silica crucibles were found to be satisfactory, platinum crucibles were chosen for all of the immersion process optimization studies because of their ability to resist thermal shock and their much lower dissolution rate. The only effect that small amounts of platinum (e.g., 0.005%) was determined to have on Bioglass is that it gives the glass the ability to crystallize at a lower temperature. In fact, platinum in amounts of less than 0.01% by weight was added to several experimental Bioglass compositions in order to obtain crystallization of the glass at 650°C rather than the 800°C temperature normally required.

Melting of the Bioglass stock was accomplished by heating to 1300°C to 1360°C in an electric furnace with the glass allowed to remain at temperature for at least 60 minutes to allow bubbles in the melt to escape before the coating of the metal substrates. The crucible was normally kept covered to minimize the vaporization of sodium from the melt.

The composition of the cast Vitallium which was used for all the immersion process optimization work is given in Table 1. The standard substrates used in this study were 45 mm long, 6 mm diameter Vitallium rods. These specimens were sawed from 150 mm high purity Vitallium castings made in air using the lost wax process.

Oxidation of Vitallium substrates selected to be air-oxidized was accomplished by the use of an electric furnace. The test specimens were suspended by a Vitallium wire into the hot zone of the furnace with a platinum/Pt-Rd thermocouple used to measure the temperature at that location. A Jelcraft HT furnace* was utilized for those specimens which were oxidized in a controlled oxygen pressure. This type of a furnace is typically used in dental laboratory practice to fire porcelain-to-metal crowns, and is capable of providing a vacuum of 30 inches of mercury or better (lower than 1 torr pressure).

Attempts to degas the Vitallium substrates prior to immersion were carried out in a MRC bell jar set-up** with a diffusion pump capable of obtaining pressures of lower than 10^{-5} torr. Vitallium rod specimens to be degassed or heat treated were placed in a 3 inch long ceramic boat and nichrome wire ribbon wound around the boat from end to end to provide uniform heating. A powerstat was regulated so that a maximum of 10 amps flowed through the wire during heating. A Micro optical pyrometer*** was used to monitor the temperature of the ceramic boat. Nine hundred degrees centigrade (900°C) was the maximum temperature obtained with this set-up, with a vacuum of better than 10^{-5} torr being easily reached for degassing purposes.

*J. F. Jelenko and Co., New Rochelle, NY

**MRC Manufacturing Corp., Orangeburg, NY

***Pyrometer Instruments Co., Bergenfield, NJ

Thermal Expansion Measurements

Knowledge of the thermal expansion coefficients of Vitallium and Bioglass is important in estimating the magnitude of the interfacial stress which occur during cooling due to the expansion mismatch of the two materials. An Orton Automatic Recording Dilatometer* was used to obtain the thermal expansion coefficients of the glass and metal. The standard 2 inch specimens used for test purposes were obtained by casting 6 inch long, $\frac{1}{2}$ inch diameter glass rods in a graphite mold. A 2 inch section of the casting free of bubbles was sawed and polished down to exactly 2.00 inches. Each glass specimen to be measured was placed in the dilatometer between two platinum contacts. The specimen was heated at a prescribed rate and the increase in length with temperature was plotted on a chart.

A silica correction factor can be included in the plot of the temperature-expansion relation in order to compensate for the thermal expansion of the glass specimen holder. In order to check the calibration of the dilatometer, a Lucalox (alumina) bar was first tested on an identical Orton dilatometer at General Electric in Cleveland. The same specimen was then run in Gainesville using the silica correction factor in one case and without this factor in another case. Comparison of the results of these tests showed that a correction factor was necessary, but one smaller in magnitude than the normal machine correction factor.

*Edward Orton, Ceramic Foundation, Columbus, OH

A 2-inch Vitallium test specimen was prepared so that a direct comparison of glass and metal thermal expansion coefficients could be made. A section was cut from a standard cast Vitallium rod and the ends of the two pieces were polished until the length was exactly 2.00 inches. This specimen was run using a procedure identical to the one used for measuring the thermal expansion of the glass specimens. Direct comparison was obtained by placing the plot of one temperature-expansion curve over the curve for the other material, with the main region of interest being from 500°C down to room temperature.

Microscopes and Specimen Preparation Techniques

Both reflection and transmitting optical microscopes were used for the examination of sectioned and polished Bioglass-coated Vitallium specimens. All specimens prepared for examination using an Olympus* reflection microscope were first mounted in PMMA, then polished using 180, 320, 400, and 600 SiC paper followed by 6 μm and 1 μm diamond paste. A Nikon** transmitting microscope was used to examine the thinly sliced Bioglass-Vitallium implants surrounded by bone. The bone-implant specimens were prepared by first drying in a series of alcohol solutions, then embedded in polymethylmethacrylate and sliced into 300 μm sections using a wafering saw with a low concentration diamond blade. Each section was ground to 150 μm using a precision swivel-head grinder. The thin sections were then cemented to a glass

*Vanox, Olympus Optical Co., Tokyo, Japan

**Biphot, Nikon, Nippon Kogaku, K.K., Tokyo, Japan

slide and ground to 50 μm . A polychromatic stain was used to prepare the tissue for microscopic observation.

A JEOL* scanning electron microscope was used to obtain high-magnification, high-resolution photomicrographs of oxidized metal surfaces and metal and glass interfacial fracture surfaces. Specimens examined by the SEM were in an unpolished condition and were coated with approximately 50 $\text{\AA}$ of gold-palladium by vacuum deposition. Specimens were fixed to the holder by silver conductive paint. Typical excitation voltage was 25 KV with the SEM image formed by secondary electrons. A 100 μm aperture was used to get better depth of field at magnifications of 1000 or less.

Compositional Analysis Techniques

Auger electron spectroscopy (AES) has been found to be a valuable tool for surface analysis of materials because the limited escape depth of the Auger electron restricts the analysis to only the surface layer (50 $\text{\AA}$ or less). Auger electron spectroscopy is also useful for detection of elements of low atomic number (e.g., oxygen). In recent studies, AES has been used in conjunction with ion milling to determine the variation in composition with the depth from the surface for Bioglass and other materials.⁴³⁻⁴⁶

Auger electron spectroscopy measurements in this study were made using a Physical Electronics Thin Film Analyzer** in a residual vacuum

*JM-35C, JEOL, Ltd., Tokyo, Japan

**CMA 10-155, Physical Electronics Industries, Inc., Edina, MN.

pressure of 2×10^{-8} torr. An electron beam of 3 KeV with a diameter of about 600 μm (defocused condition) was used. Total beam current was measured using a Faraday cage. Sputter profiling (ion milling) was accomplished using 2 KeV argon ions with the chamber back filled to 5×10^{-5} torr.

Vitallium specimens analyzed by AES to determine oxide layer composition were 5 mm-thick slices taken from the test rods and sawed on one end to allow clamps to hold the specimen in place on the carousel. Most of the Bioglass specimens examined by AES were the curved glass coatings which had been stripped off the metal rods during shear testing. These small glass pieces were attached to metal tabs on the carousel by the use of silver conductive paint. A partial coating of silver paint was also applied to the extremities of the top surface of the glass to minimize charging during electron bombardment.

A plot of the derivative of the number of counts versus the electron energies was obtained for each time period as the electron beam scanned the specimen (as in Fig. 1). Each plot was obtained for a different time of ion milling, and this time was correlated to depth from the surface by using 50 $\text{\AA}$ per minute as an estimate of the sputtering rate. Characteristic peaks of each element of interest were selected (Fig. 1) and measured to determine the occurrence of the particular element in the area analyzed by the beam. A normalization factor was calculated for each element so that peak height could be converted into a number which could then be compared directly with similar

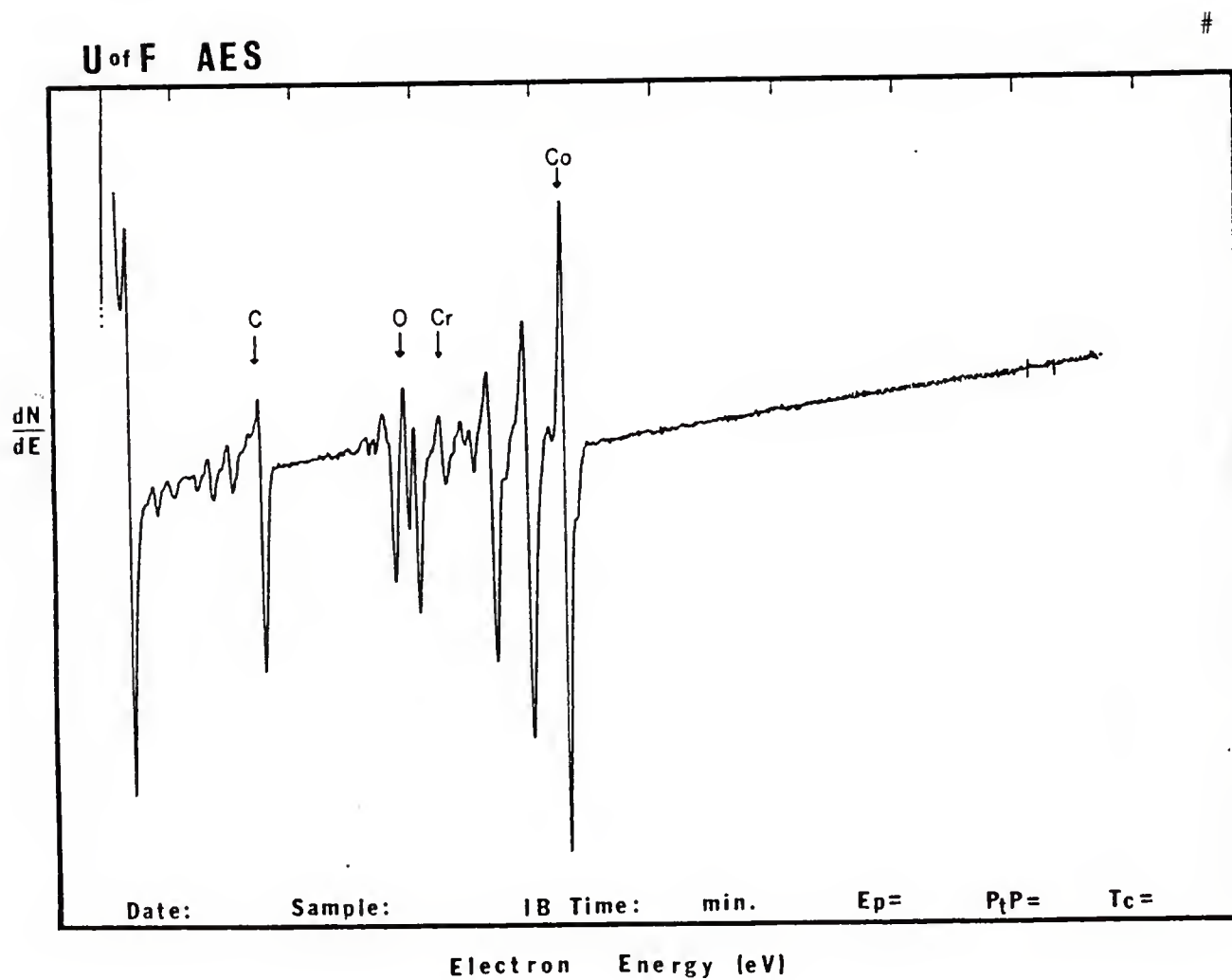


Figure 1. Typical AES analysis of Vitallium surface showing peaks selected for measurement.

numbers obtained for other elements in order to get relative occurrence of each. The volume fraction ratio of Co to Cr was determined by converting the ratio of the weight percentages (65/28) into the ratio of the atomic percentages (2.63). The ratio of selected peaks of Co and Cr obtained under equivalent conditions was found to be 34.6/15.5 or 2.23. Therefore each Co measurement, for example, could be normalized by multiplying by 2.63/2.23 or 1.18. Because of differences in specimen placement and beam angle, peak heights could not be compared directly from one specimen to another without first normalizing the data.

An electron microprobe* (EMP) was used to determine the extent of the diffusion of ions across the metal-glass interface. The microprobe has generally a better quantitative capability than AES, but is limited in its ability to analyze points close together (i.e., less than 5 μm). Also, the escape depth for X-ray is much larger than that for the Auger electrons, so EMP is not as useful for the analysis of surfaces.

Specimens to be analyzed by the EMP were first polished to 600 grit SiC, then to 1 μm diamond paste. The polished specimens were coated with approximately 100 Å of carbon by vacuum evaporation and electronically connected to aluminum discs by the use of silver conductive paint. The coated specimens were placed in a stage inside the EMP vacuum chamber which was moved perpendicular to the electron beam at a specified rate of 20 μm per minute during analysis. An

*Electron Probe X-ray Microanalyzer, Model MS-64, Acton Labs., Acton, MA

electron beam diameter of 1 μm , a beam current of 10^{-7} amps, and a volt differential of 20 KV were typical operating conditions. An argon-methane flow proportional detector with various crystals (e.g., quartz, mica, LiF) was used to measure radiation intensities. These intensities were represented as peaks and plotted as in Fig. 2 as counts per second with a set chart speed of 20 $\mu\text{m}/\text{min}$.

Normally the microprobe can analyze points no closer than 5 μm apart because of beam size and reflection characteristics. This is a problem as the interfacial zone of Bioglass-Vitallium specimens coated by the quick immersion process is typically less than 5 μm wide. A technique commonly employed in the study of oxide layers on semiconductors was used to prepare several specimens so that more readings could be taken in the interfacial zone. Selected specimens were polished through the glass at an angle of 1° until the metal was contacted, thus increasing the surface of the oxide layer and other areas of interest in the interfacial zone. Using calculations based on the curvature of the metal away from the polished surface, the actual distance of each point of analysis from the true interface was determined.

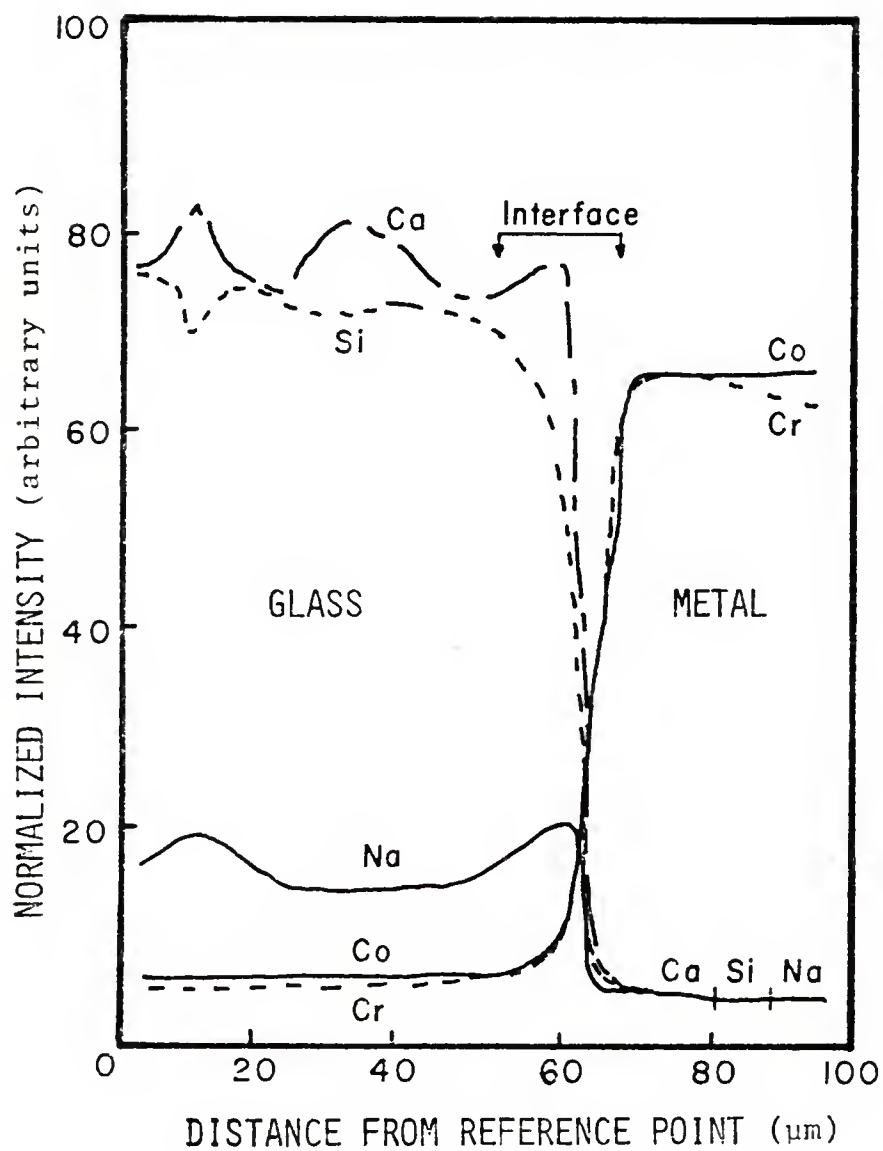


Figure 2. Typical EMP analysis of a Vitallium specimen immersion-coated with Bioglass.

CHAPTER IV BOND STRENGTH TESTING

Nature of Bond Testing

A quantitative determination of the interfacial strength should be a key factor in any study which seeks to investigate and improve glass-metal bonding. However, in many investigations of metal-glass adherence only qualitative-type tests are used. In reviewing the literature it quickly becomes obvious that there is no universally accepted testing method for measuring interfacial strength between a metal substrate and a glass coating. Various researchers appear to have developed tests which best suit their purposes, but often their results cannot be duplicated by others using similar tests. The large scatter of values reported in many adherence tests may be due to the complex nature of the glass-metal bond and indicates that measurement of true interfacial strength is difficult and is influenced by extraneous factors such as porosity at the interface.

There are several types of products or devices in which strong glass-to-metal bonding is of major importance. Three of the most important of these are commercial porcelain enamels, glass-to-metal seals in the electronics industry, and porcelain-metal crowns in dentistry. Adherence tests developed in each of these areas will be discussed in order to analyze relative strengths and weaknesses and

to determine which type of a test is most suitable for measuring the bond strength of Bioglass-coated-Vitallium specimens prepared by the immersion method.

Porcelain Enamel Tests

There are a number of ASTM tests which have been developed to judge porcelain adherence to metal:⁴⁷

1. ASTM C313-59 describes a method for testing the adherence of porcelain enamel and ceramic coatings to sheet metal. A hydraulic jack is used to push a coated sheet metal piece into a stationary steel ball at a controlled rate causing deformation of the coated test specimen. Measurements are made on the deformed area by an electronic probe to determine size of deformed area and integrity of remaining coating. This method gives no direct measurement of actual bond strength and is not applicable for metals over 2 mm thick.
2. ASTM C409-60 describes a method for testing the torsion resistance of porcelain-enameled iron or steel. Metal specimens bent to a 90° angle and coated on both sides with porcelain are twisted on a special machine until the glass first chips. The angle of twist necessary to chip off the porcelain coating is a measure of adherence when compared to similarly tested specimens.
3. ASTM C385-58 measures the thermal shock resistance of porcelain-enameled utensiles. Coated metal specimens are quenched from a selected temperature into water repeatedly until fracture of the coating occurs. This procedure is repeated at various temperatures, and the number of cycles necessary to produce fracture of the glass coating is compared to similarly tested specimens.
4. ASTM C633-69 describes a test for flame sprayed coated metal but it can also be used for porcelain enameling. In this test the coated metal piece is attached on both sides to blocks on a tensile testing machine. The composite is loaded at a controlled rate and the load required to break the porcelain-metal bond is divided by the cross sectional area to give a measure of the interfacial strength.

One of the tests most commonly used to judge the adherence of porcelain enamel to metal is the simple bend test. In this test porcelain is coated on one side of the metal strip, the coated strip is bent so that the porcelain side is put in compression, and the bending force is increased until the porcelain shatters. This test can also be set up so that the porcelain side is in tension. In either case the actual force required to fracture the porcelain is not a good measurement of bond strength, and varies greatly depending on such factors as the modulus and thickness of the metal strip. The usual means of evaluating the porcelain-metal bond using this test is to observe whether the porcelain pieces adhere well to the metal strip after fracture occurs.

King, Tripp, and Duckworth²⁶ used a falling weight test to make some of the adherence measurements for their study on porcelain-metal bonding. The test consisted of dropping a cylindrical hammer with a $\frac{1}{4}$ inch diameter ball on the end onto the back of a coated metal test specimen. Adherence was judged by calculation of the fraction of the enamel which remained on the deformed metal after impact. These same investigators also used a tensile test similar to that specified in ASTM C633-69, and were able to get quantitative measurements of bond strength up to the limit of the epoxy used (about 6000 psi).

Glass-Metal and Ceramic-Metal Seal Testing

Most of the testing of glass-metal seals have been accomplished by the use of either a tensile test or a peel test. A standard ASTM

test (ASTM F19-64)⁴⁸ has been developed for testing a glass seal between ceramic or metal (Fig. 3a). Twentyman⁴⁹ used a cup and washer test assembly and provided a tensile force to break the seal (Fig. 3b), while in a similar test, Floyd⁵⁰ used hydraulic pressure to apply the force to the seal (Fig. 3c).

All of these tests employ a tensile force normal to the glass-metal interface, but in many cases measurement of shear strength by a force parallel to the interface would be more valuable. A case in point would be the measurement of the force necessary to pull a metal lead-through wire out of its glass seal.

Peel tests are also used quite frequently to estimate the bond strength of glass to metal. One such test involves sealing a thin metal strip to a glass piece, then measuring the force which is necessary to initiate and/or continue the peeling of the metal from the glass. Cole and Hynes⁵¹ developed an unusual test (Fig. 3d) in which pressure is applied by plungers which cause the rubber discs to force the sealed piece outwards. The force necessary to break the seal is taken as a measure of its bond strength. This test, like some of the others mentioned, gives only an indirect measurement of bond strength, and it is useful only for comparison of similar specimens.

Testing of the Porcelain-Metal Crown

Some of the more sophisticated tests for measuring glass-metal interfacial strength have been developed for testing the integrity of the dental porcelain-fused-to-metal crown. A high metal-glass bond

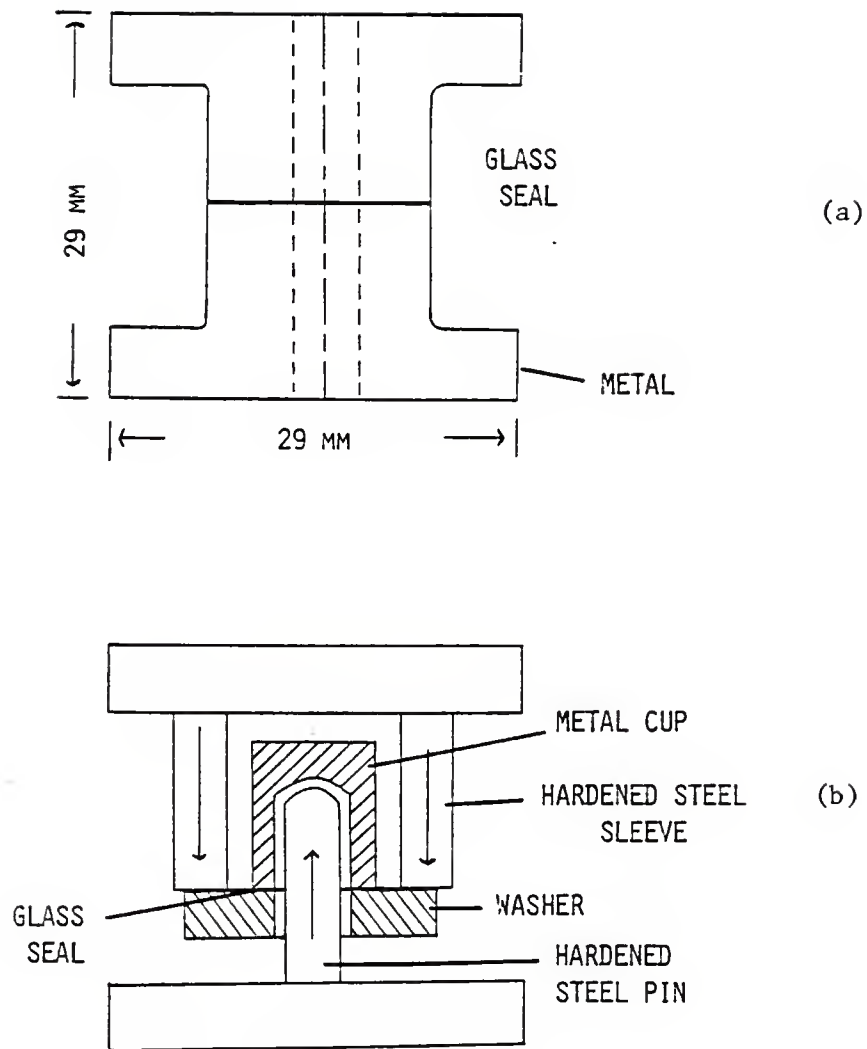
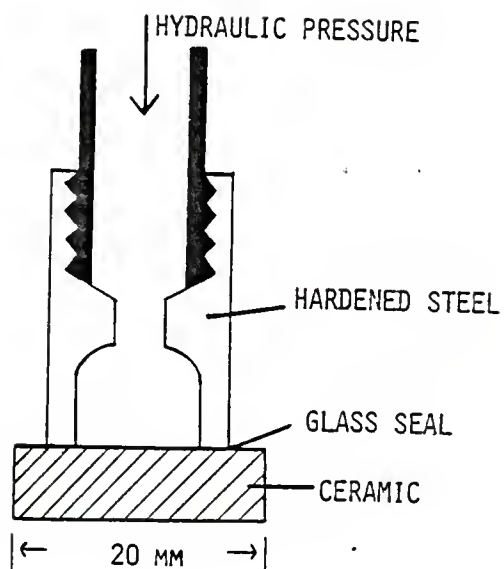
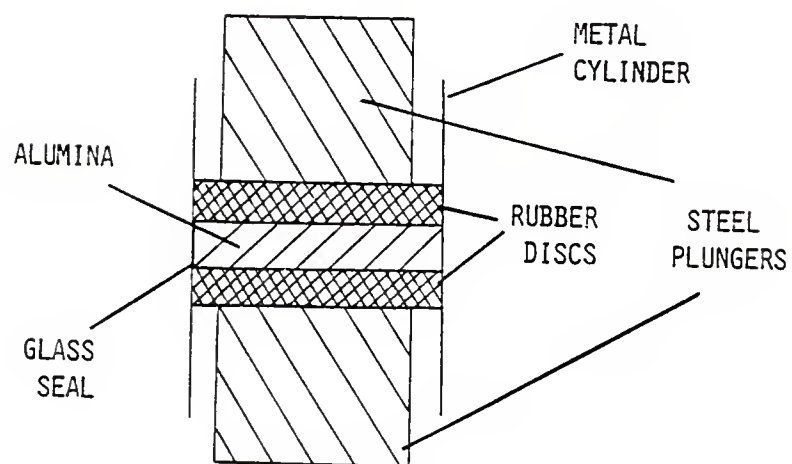


Figure 3. Tests of glass-metal seal strength.

- (a) ASTM tensile test assembly
- (b) Cup and washer tensile test assembly



(c)



(d)

Figure 3. - continued

- (c) Hydraulic test of seal strength
(d) Metal-glass-ceramic seal test

strength is necessary to assure proper functioning of this device when it is subjected to the complex stresses which occur during mastication.

One of the most commonly used bond strength tests for porcelain-metal crowns was developed by Shell and Nielsen.⁵² In this test porcelain is built up around a 14 guage wire (1.63 mm diameter) to a depth of 2.5 mm (Fig. 4). The amount of force required to pull the wire (rod) out of the porcelain is recorded, and the known surface area of the wire which is covered by the porcelain is used to find the interfacial strength (force/unit area). The porcelain-metal bonding area is kept small so that the interfacial bonds will break before the yield strength of the wire is reached. One drawback to use of this type of test is that the porcelain is typically under compression so the gripping force of the porcelain "collar" may add to the observed bond strength.

Lavine and Custer⁵³ used a bend test which consists of coating porcelain on a flat metal strip and bending the composite so that the porcelain side is in tension. The major deficiency in this test is that the maximum tensile stress in the composite is at the surface of the porcelain so failure is likely to start there. The glass-metal bond area is under much less tensile stress as it is near the neutral plane where the stress is zero, so true interfacial strength is not measured by this test.

Anthony et al.⁵⁴ and Leone and Fairhurst⁵⁵ modified the Shell-Nielsen test by removing porcelain from the end of the rod (wire), thus eliminating a source of error arising from differential shearing

stresses. These investigators also used a coated-strip bend test similar to that of Lavine and Custer to observe the fracturing of the coating in tension.

Knap and Ryge⁵⁶ used a standard, threaded metallurgical tensile bar coated with porcelain in a test of porcelain-metal bonding. They coated porcelain on the center of the bar, machined off the excess porcelain so that a cylindrical diameter remained, and loaded the coated specimen in tension until the porcelain fractured. The load at fracture was taken to be the point at which circumferential cracks first ringed the specimen. This was not an exacting test, as cracks sometimes started near the threads and around the ends of the coated area, and many specimens had to be discarded. Also, reported values (Table 4) were much too high to be true interfacial strength measurements, as the modulus and strength of the metal bar contributed to the final test values.

Sced and McLean⁵⁷ developed a bond strength test to overcome some of the problems inherent in the Shell-Nielsen and other tests. A conical-ended test piece is coated with porcelain and pulled in tension until fracture (Fig. 5a). The 90° cone allows the angle of fracture in the porcelain to approximate the direction of maximum shear stress, with interfacial strength being the load divided by the porcelain-metal area.

Kelly, Asgar, and O'Brien⁵⁸ developed a tensile test for measuring porcelain-metal adherence (Fig. 5b), but found that bond strengths measured by this test were only half of those of the Shell-Nielsen

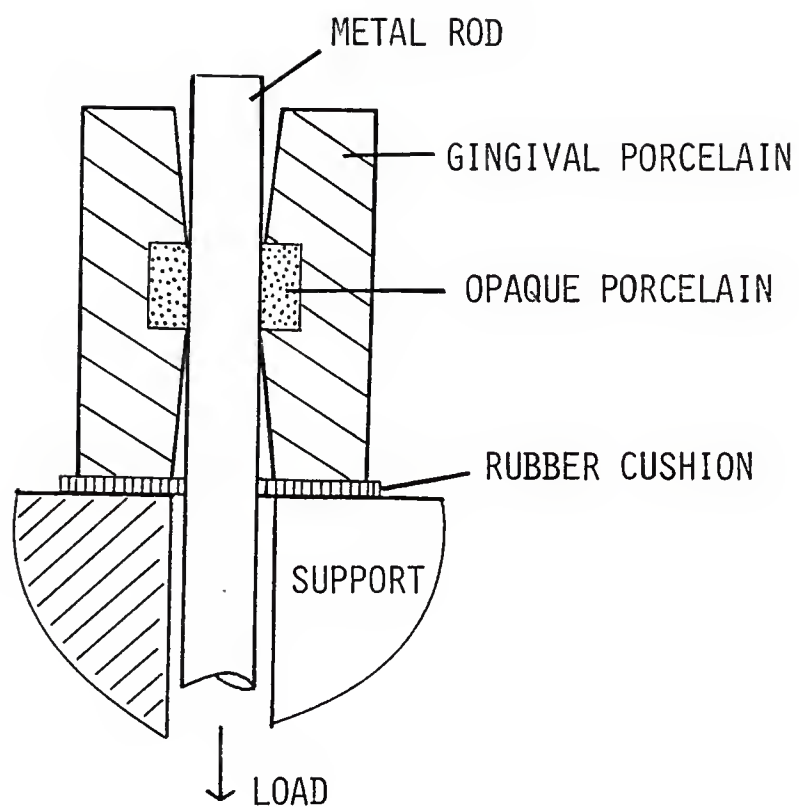


Figure 4. Shell-Nielsen shear test.

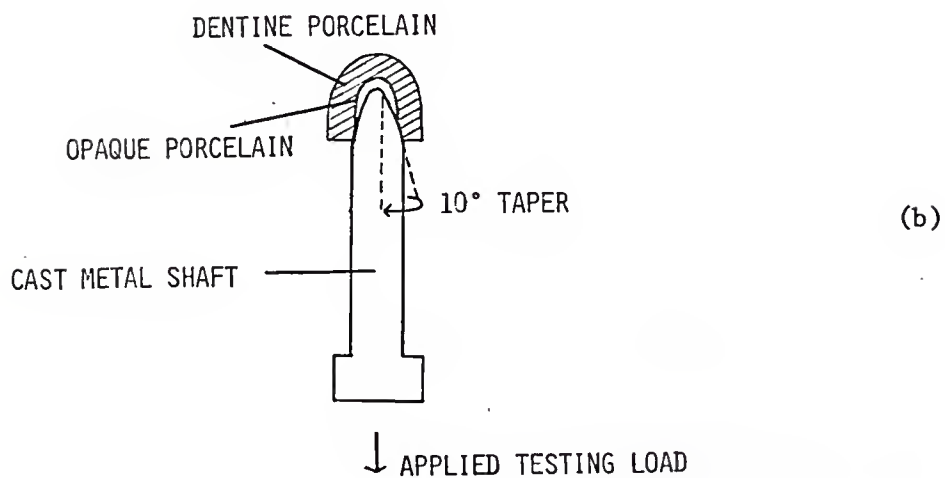
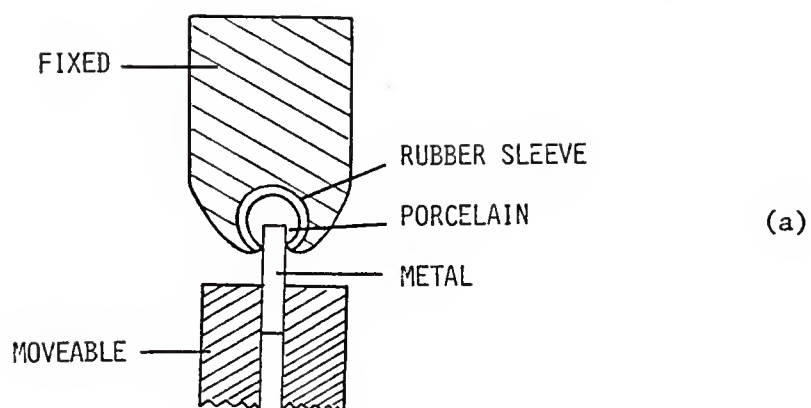


Figure 5. Dental porcelain-metal bond strength tests.

(a) Sced and McLean's test.

(b) Kelly, Asgar, and O'Brien's test.

test due to the primarily tensile mode of failure (Table 4). Nally⁵⁹ measured the tensile strength of porcelain-metal bonds by a rupture test in which two small metal cylinders were joined end-to-end by baking a layer of porcelain in between. However, an interfacial strength could not be measured as all fractures occurred in the porcelain, not at the porcelain-metal bond. Johnson et al.⁶⁰ used a similar tensile test in which two rods of cast gold were held in axial alignment and joined by porcelain. The problem with this type of test is keeping the metal rods in perfect alignment during firing, as misalignment contributes to the large scatter commonly observed in the data.

Suitability of Tests for Measuring Bioglass-Vitallium Bond Strength

As can be seen from a review of the literature, there are a number of different methods used to estimate the interfacial strength between a glass and metal. Bond strength results of tests made on similar systems (e.g., porcelain-to-gold) often vary widely between the different testing methods. This is due partly to the fact that these tests are actually measuring different parameters. For example, it makes a great deal of difference whether the interface is put in tension, compression, shear, or torsion during testing. If the applied load is parallel to the interface, then interfacial roughness is an important factor (e.g., the glass "peaks" may be sheared off easily). If a force normal to the interface is applied, the glass-metal junction is in tension with a separating force tending to

Table 4

Glass-Metal Bond Strengths from Various Researchers

Source	Test	Bond	Average*	Range or Std. Dev.
Johnson ⁶⁰ (1956)	2 rods-joined	gold-porcelain	393	273-494
Nally ⁵⁹ (1968)	2 cylinders-joined	gold-porcelain	256	
Sced and McLean ⁵⁷ (1972)	shear	gold-porcelain	284	
		Co-Cr-porcelain	226	
		Ni-Cr-porcelain	242	
Lavine and Custer ⁵³ (1966)	bent strip	gold-porcelain	16	+25%
Knap and Ryge ⁵⁶ (1966)	around tensile bar	gold-porcelain	2348	499
Anthony et al. ⁵⁴ (1970)	wire pulled out	gold-porcelain	966	
Leone and Fairhurst ⁵⁵ (1967)	wire pulled out	gold-porcelain	934	20
Vickory and Badinilli ⁶¹ (1968)	wire pulled out	gold-porcelain	1050	3%
Shell and Neilsen ⁵² (1962)	wire pulled out	gold-porcelain	720	11%
King et al. ²⁶ (1959)	tensile	iron-enamel	419	
Kelly et al. ⁵⁸ (1969)	shear, tensile	gold-porcelain	356	7.0
		(non-ox) gold-porcelain	200	16.9

*Test results in Kg/cm²

overcome the mechanical interlocking. If the test introduces too high a level of tensile stress in the glass coating, the glass will fracture before the glass-metal interface fails.

A number of the most commonly used tests from the literature are given in Table 4 along with reported values of glass-metal bond strengths of various composites. The great variability in the nature of the test methods is revealed by comparing bond strength results obtained from similar systems. For example, average bond strengths for gold-porcelain range from 16 Kg/cm^2 to 2348 Kg/cm^2 , a factor of almost 150. Also, the range of scatter in the data is quite large in many cases, as is commonly observed in the testing of brittle materials.

Some investigators have attempted to develop a test which gives the highest possible bond strength for a given system. This is often accomplished by negating the effect of flaws such as microcracks or porosity which occur at the interface or throughout the glass. This approach is not always desirable as one of the primary objectives of the test should be to evaluate the strength of the glass-metal interface under conditions which are similar to those occurring in actual service. As the presence of flaws has a pronounced effect on the failure of composites and brittle materials, their effect on bond strength should be evaluated by the test and not minimized except in cases where fracture tends to occur in the glass coating rather than at the interface.

The use of the immersion technique as a coating method greatly restricts the type of test which can be used to give a quantitative

measurement of glass-metal bond strength. In reviewing the available adherence tests to evaluate their suitability for testing immersion-coated Bioglass-Vitallium specimens, the following observations can be made:

1. A bend test which puts the glass layer in either tension or compression is not a quantitative test for the determination of bond strength and is not satisfactory for any type of coated specimen.
2. The joining of two metal rods by holding them in alignment during immersion is impractical as the entire length of one rod and the alignment fixture will be covered with glass. Also the extensive machining required to remove excess glass would introduce additional flaws into the glass coating.
3. The threaded tensile bar (as described by Knap and Ryge)⁵⁶ could be immersed in Bioglass with one end coated with a substance (e.g., colloidal graphite) which would not allow the glass to wet the metal. However, the test method itself is undesirable because it does not measure interfacial strength. In this test the strength of the substrate metal is of primary importance, which accounts for the fact that bond strengths obtained by this method are a factor of 10 higher than other adherence tests.
4. The use of a tensile test such as described by King et al.²⁶ would require the machining or grinding of the excess glass off the immersed end of the metal rod, and the use of an epoxy which would bond strongly to both metal and glass. Even if a successful means of fastening (e.g., epoxy) is used, this test measures only the bond strength for a load applied normal to the interface and not the potentially more severe case in which the load is applied parallel to the interface.
5. A pull out shear test such as the one developed by Shell and Nielsen is one of the few testing methods which can be adapted for making quantitative bond strength measurements on immersion coated specimens using a load parallel to the interface. A minimum amount of machining would be required to prepare immersion coated specimens for testing by this method or a similar technique.

The Push Thru Shear Test

A "push-thru" shear test similar to the one used by Shell and Nielsen was developed in order that a quantitative evaluation of the glass-to-metal bond could be made. To prepare specimens suitable for testing, Vitallium rods 45 mm long and 6 mm in diameter are coated to approximately 2/3 of the total length (30 mm) with Bioglass. The glass is removed from one end with a diamond saw and grinding tool so that a bare metal section is left (Fig. 6). Enough glass is removed so that there is exactly a 25 mm coated section with a flat shoulder remaining. Precautions must be taken to insure that the ends of the metal rod are cut perpendicular to the axis, and that the glass shoulder is exactly flat and perpendicular to the axis of the rod so that the full measured shear force occurs at the glass-metal interface.

The shear force is provided by an Instron testing machine* used in the compression mode. The testing fixture consists of 2 steel cylinders, one of which has a hole through the center which is slightly greater than 6 mm (the diameter of the coated metal rod). The prepared test specimen is placed so the flat glass shoulder rests on the surface of the steel cylinder with the bare end of the rod protruding down into the shaft. The other section of the test fixture holds the specimen perpendicular so the Instron forces the two sections to come together at a rate of 1.25 mm/min. The load required to strip the glass coat off the metal rod is recorded and divided by the total surface area

*Table Model-TM, Instron Corp., Canton, MA

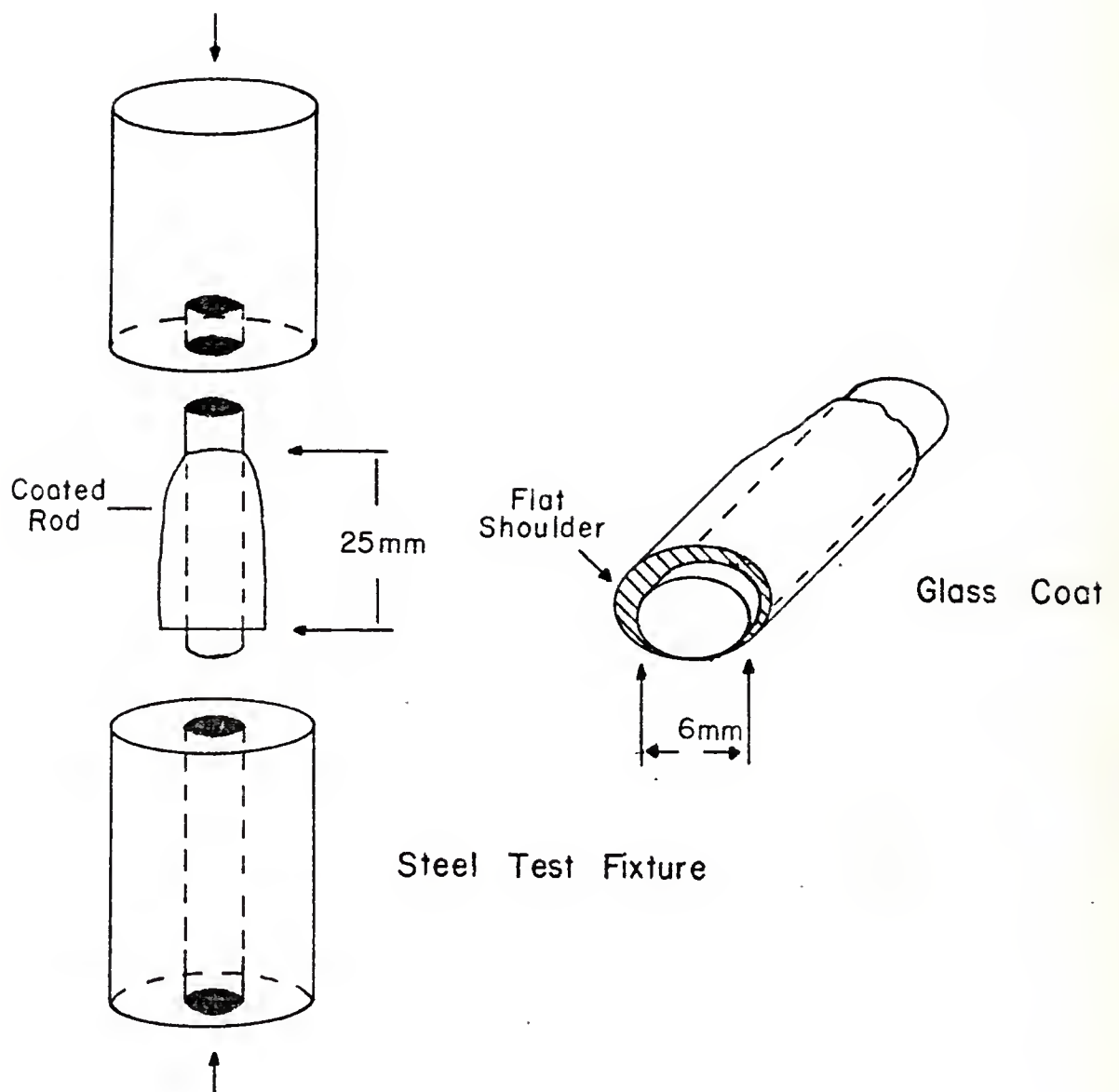


Figure 6. The push thru shear test.

(475 mm²) to obtain the shear stress. Other specimens with one-half and one-fourth this total surface area are also tested to determine if similar values of shear strength are obtained for a range of surface areas.

A typical Instron test on a Bioglass-Vitallium specimen produces a stress-strain curve which is linear from zero until the point of fracture. This linear stress-strain behavior is typical of a brittle material such as glass, and indicates the lack of occurrence of such mechanisms as plastic deformation at the glass-metal interface. As the load is applied to the specimen, the stress-strain (time) plot follows a straight line which is representative of the elastic range of the composite. There is sometimes a slight dip or chatter in the curve just before fracture, but usually the glass coating is stripped off the metal almost instantaneously after fracture starts.

Another test which has been used in previous work involves quenching the glass coated rods from a range of temperatures to determine the maximum temperature change the glass-metal interface can endure without fracturing. The numerical shear stress needed to fracture the bond can be estimated by the following relation: Shear stress = $1.33 \bar{E} \Delta\alpha\Delta T$ where $\bar{E}$ is the average elastic modulus, $\Delta\alpha$ is the difference in thermal expansion coefficients between the metal and glass, and ΔT is the temperature change necessary to fracture the glass at the interface.⁶² The greater the change in temperature that the specimen can withstand without fracturing, the higher is the estimated strength of the glass-metal interface. Results from this

test can be compared directly to those from identical specimens tested by the "push-thru" shear test and a correlation between the two test methods can be determined.

CHAPTER V THE METAL OXIDE-METAL INTERFACE

Introduction

During the initial testing of the bond strength of Bioglass-coated-Vitallium specimens, the glass was observed to fracture off the metal leaving a clean, shiny metal surface. Prior to immersion in the molten glass, the metal surface had been covered with an oxide layer which was a dull green, gray, or blue color. Examination of the glass pieces revealed that the surface which had been next to the metal was covered with a thin gray, metallic layer. These results suggested that the metal oxide-to-metal bond might be the weakest link in the glass-metal interface.

The oxidation of the metal substrate to achieve satisfactory wetting of the molten glass is one of the most important factors in establishing the proper conditions for good bonding between glass and metal. Variables of the oxidation process (such as temperature and time of oxidation) can be controlled so that an oxide layer of an acceptable thickness is formed on the metal. But proper thickness may not be enough, for in some cases conditions must be controlled so that the strength of the bond between the metal and its oxide is maximized.

The glass-oxide bond is generally strong in a well designed system as the molten glass absorbs part of the oxide layer as it wets the metal

substrate. However, many metals such as iron form only a weak bond with their oxide under normal conditions. Therefore, in commercial porcelain enameling of steel it is desirable to continue heating until the iron oxide layer is completely dissolved in the molten glass. In this case there are special mechanisms, such as the reduction of adherence oxides in the ground coat, which continue the oxidation of the iron substrate and keep the interface saturated with the metal oxide. In other cases, however, these mechanisms are not available and care must be taken to leave a thin oxide layer undissolved by the glass so that interfacial equilibrium is maintained. These are the situations in which it is important to have a strong metal-metal oxide bond for maximum adherence of the glass coating to the metal.

Oxidation of Cobalt-Chromium Alloys

An understanding of the oxidation process of cobalt-chromium alloys is important in determining if the Bioglass-Vitallium bond strength can be improved by proper control of the oxide layer. Oxidation of cobalt alloys containing chromium is similar to that of stainless steels and nickel-chromium alloys. If these alloys contain sufficient chromium (15-20%) a protective layer of Cr_2O_3 is formed which limits further oxidation. Thus these alloys are used for a variety of high temperature applications such as turbine blades for jet engines and as heating elements.

In cobalt-chromium alloys, CoO usually forms on the metal surface first during heating because of the higher initial mobility of the Co^{2+}

ion. The oxidation process starts by electrons moving to the surface of the metal where they ionize the chemisorbed oxygen molecules. This sets up a condition in which the metal ions can now move to the surface to meet the O^{2-} ions more freely because of the influence of both chemical and electrical potential gradients. The defect chemistry of the alloy is an important part of the oxidation process, as electrons initially hop between normal lattice sites and electron holes followed by metallic ion diffusion through the cation vacancies (the cobalt alloy is a metal-deficient p type semiconductor). Even though the presence of some high valence impurities as chromium may accelerate the oxidation rate, Wright and Wood⁶³ found the rate of oxidation of cobalt-chromium alloys to decrease as the chromium content was increased to over 15%.

During the oxidation process, the migration of the metal cations to the surface causes the movement of vacancies in the opposite direction. These vacancies tend to stop and coalesce at the oxide scale-metal interface so that voids are formed which may be a major cause of the weak bonding between the oxide and metal. Thus thicker oxide layers which have been oxidized for longer times are more likely to be poorly bonded to the metal.

The scale (oxide layer) of a cobalt-chromium alloy is predominately Cr_2O_3 if the alloy contains at least 15% chromium. Elements such as chromium, aluminum, and silicon tend to be selectively oxidized because of their high affinity for oxygen. However, because the initial diffusion of Co^{2+} is higher than Cr^{3+} , the outer oxide layer of cobalt-chromium alloys typically consists of CoO with some spinel particles

(CoCr_2O_4). If there is sufficient chromium in the alloy (e.g., 20%), islands of Cr_2O_3 formed initially will eventually develop into a continuous layer. This "healing" or protective layer of Cr_2O_3 slows down the diffusion of metal and oxygen ions so the oxidation rate is greatly reduced after its formation.⁶⁴

Comparison of Cobalt-Chromium with Other Alloys

As cobalt-chromium, iron-chromium (stainless steel), and nickel-chromium are often used in similar applications, a comparison of the oxidation behavior of each may be useful in predicting which should form the strongest bond with its oxide, and thus have more potential for forming a strong glass-metal composite.

Unalloyed cobalt oxidizes at a rate of 25 times that of nickel.⁶⁵ For cobalt alloys containing sufficient chromium, the growth rate of CoO is reduced but is still higher than that of NiO or Fe_2O_3 in similar alloys. This means that an outer layer of unprotective CoO is formed faster and vacancy diffusion to the scale-metal interface is greater, potentially causing more extensive void formation and reduced oxide-to-metal bonding in a cobalt-based alloy.

The alloy interdiffusion coefficient determines how rapidly the chromium (which is the preferentially oxidizing element) can be supplied to any surface or developing healing layer. The cobalt-chromium system has a lower alloy interdiffusion coefficient than the nickel-chromium system, thus the healing Cr_2O_3 layer takes longer to form and the cobalt-chromium alloy may oxidize more extensively before its formation. Also

it is more difficult to form the protective Cr_2O_3 layer on cobalt-chromium alloys because the growth rate (and hence encroachment rate) of CoO is higher than that of NiO or Fe_2O_3 .⁶⁶

The oxygen solubility and diffusivity in an alloy determine its internal oxidation characteristics, with a high value causing more internal oxidation. Iron-chromium alloys, because of their lower oxygen solubility, tend to form a protective Cr_2O_3 layer closer to the surface than cobalt-chromium or nickel-chromium alloys. Thus, the oxide layer on cobalt-chromium and nickel-chromium alloys is generally thicker than that formed on stainless steel under the same conditions. Thicker oxide layers generally cause more spalling of the oxide during cooling, but Wood⁶⁶ found that a nickel-chromium alloy with a slightly thicker oxide layer had better scale adherence than cobalt-chromium or iron-chromium alloys because a more irregular and interlocking alloy-oxide interface was obtained under identical conditions.

It appears that a strong bond between cobalt-chromium and its oxide is more difficult to achieve than between nickel-chromium and iron-chromium and their oxides because of the values of such variables as bare metal oxidation rate, alloy interdiffusion coefficient, and oxygen solubility. This means that oxidation conditions must be more tightly controlled for cobalt-chromium alloys in order to get a satisfactory degree of bonding between the metal substrate and its oxide prior to coating with glass. There is little direct comparison available as to which of these three alloy systems forms the best bond with glass or ceramic coatings. In one instance, however, McLean⁶⁷ found

that nickel-chromium alloys formed a strong bond with dental porcelain, while cobalt-chromium alloys coated with porcelain failed at the metal-metal oxide interface.

Changing the Nature of the Metal-Metal Oxide Bond

There are a number of variables which can play an important role in determining the nature of the bond formed between the metal and its oxide layer. The optimization of each of the factors which can be varied for the Vitallium oxidation process may be important in achieving the ultimate goal of a strong glass-metal bond.

The addition of other elements to cobalt-chromium alloys has been shown to increase oxidation resistance, enhance the formation of a protective layer, and increase oxide-to-metal bonding. Kumar and Douglas⁶⁸ found that the addition of silicon (e.g., 4%) to alloys containing chromium caused the formation of a more protective scale but imparted brittleness to the alloy. Wood and Shott⁶⁹ found that the addition of aluminum to cobalt-chromium alloys formed an Al_2O_3 layer which was more protective than Cr_2O_3 because of less volatilization at higher temperatures. Other elements with lower oxygen affinity have a lesser effect on the nature of the oxide layer formed. In cobalt-chromium alloys, the presence of molybdenum in amounts up to 10% (Vitallium has 5.5% Mo) has been shown to have little effect on the oxidation behavior.⁷⁰

The most promising means of strengthening the oxide-metal bond in cobalt-Chromium alloys is by addition of small amounts of rare earth elements. Stringer and Wright⁷¹ added 3% Y_2O_3 (by volume) to a cobalt-chromium alloy and observed a marked decrease in oxide layer growth and an

increase in scale adherence. Allam et al.⁷² added hafnium and HfO_2 to a similar alloy and found that the adherence of the oxide to the metal was greatly increased and was superior to alloys containing yttrium and cerium additions. Wright et al.⁷³ added 1% ThO_2 to a nickel-chromium alloy and found that increased scale adherence was due partly to the formation of "keys" of rare earth oxides which anchored the scale to the metal. It has been observed by various researchers that the improved adhesion of oxide layers on cobalt-chromium and similar alloys by the addition of as little as 0.1% of a rare earth element or oxide is due to 1) a slower oxidation rate, 2) keying on internal oxides, 3) a convoluted alloy-oxide interface, 4) the increased mechanical properties of the alloy-scale composite, 5) smaller oxide grain size and 6) the ability of the internal oxide particles to absorb inward flowing vacancies (so no voids are formed).

Cold working of a cobalt-chromium alloy before oxidation can assist in the formation of a protective oxide layer by increasing the alloy interdiffusion coefficient so that the Cr_2O_3 layer forms more quickly. Also, the cold-worked alloy is a better sink for vacancies so void formation at the oxide-metal interface is reduced and increased adherence of the scale results. On the negative side, however, spalling of the oxide layer may occur more readily because of the higher residual stresses in the alloy after the cold working operation.⁶⁶

Reduction of the oxygen pressure during the oxidation process tends to form a more adherent scale by favoring the formation of the Cr_2O_3 layer. Because of the lower external oxygen pressure, the

oxygen flux into the alloy is reduced whereas the flux of the oxidizing element to the surface remains unchanged. This tends to cause the formation of a compact protective layer on the surface rather than an internal oxide which only later coalesces to form the healing layer. Thus, it may be advantageous to form the oxide layer in a low oxygen environment to establish a strong protective layer before heating the alloy to an air atmosphere. Wood⁶⁶ found that an alloy which was brought to temperature in a partial vacuum, cooled, and then reheated in air, oxidized very little because a thin adherent Cr_2O_3 layer was initially established. Eoer and Meier⁷⁴ observed that specimens oxidized at a low oxygen pressure developed smoother, more uniform scales than identical specimens oxidized at normal atmosphere pressure.

Of the three principal ways of increasing oxide adherence, the use of a reduced oxygen pressure to form a tight, protective Cr_2O_3 layer appears to be the most desirable for Vitallium. A typical sequence would be to heat the Vitallium substrate in a low oxygen atmosphere, cool to room temperature, then preheat in air or a controlled atmosphere prior to immersion in Bioglass.

The amount of mechanical work in the Vitallium specimen cannot be altered because the alloy is either in the wrought form for high strength applications or has been cast to a precision shape for such uses as dental crowns. However, operations such as grit blasting induce a certain degree of cold work to the surface layer of the metal, and thus direct comparison can be made between the oxide layer formation on a grit blasted specimen as compared to an electropolished or untreated specimen.

Improvement of oxide adherence to Vitallium by major alloy modifications is not feasible at this time. Vitallium has been certified in extensive clinical tests and has been used for many years for medical and dental applications. Any significant change in its composition would require a recertification procedure, which usually involves years of animal and human tests. A minor modification, such as the addition of less than 1% of a rare earth element, might require only minimal tests for recertification. As this approach appears to be most promising for major strengthening of the oxide-metal bond, future studies for the development of new Vitallium alloys containing these elements are recommended. However, the major objective of this research is to optimize the bond between Bioglass and Vitallium without changing the composition of either, so any alloy modifications will be left for future work.

Analysis of the Oxide Layer on Vitallium

Both scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) were utilized to characterize the surface of the Vitallium after oxidation. Scanning electron microscopy was used to visually determine the effect of the pre-immersion oxidation treatment on the topography and nature of the substrate surface. Figure 7 shows a grit blasted specimen a) before oxidation, b) after oxidation at 600°C for 10 min., and c) after oxidation at 800°C for 3 hrs. There is little discernable difference at 1000X between the unoxidized specimen and the one oxidized for only 10 min. at 600°C. The magnitude of the oxide layer in Fig. 7b is much less than the peak-to-valley height of

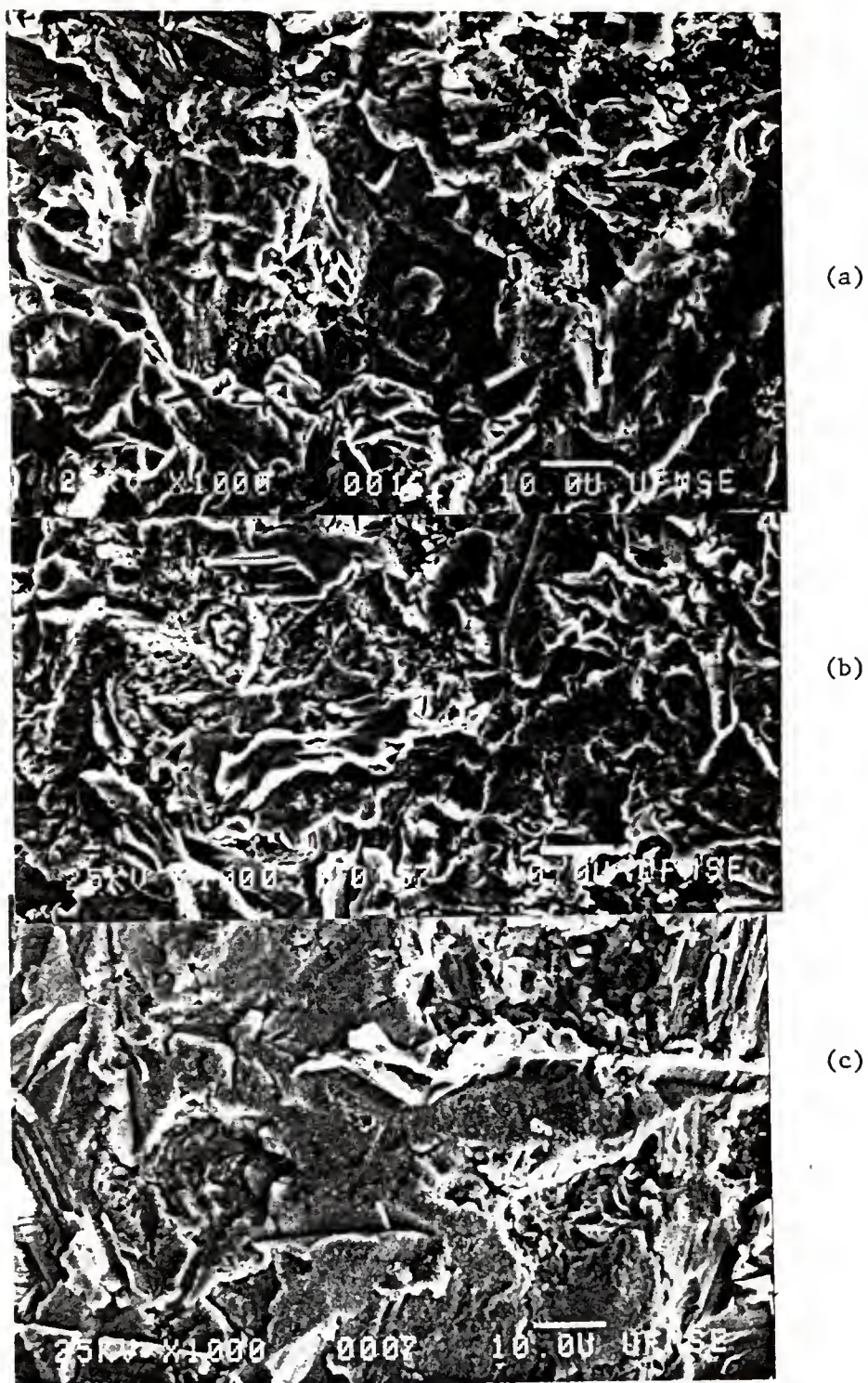


Figure 7. Scanning electron micrographs (1000X) of grit blasted Vitallium surfaces.

- (a) Unoxidized
- (b) Oxidized at 600°C for 10 min.
- (c) Oxidized at 800°C for 3 hrs.

the surface profile resulting from the grit blasting operation. However, after 3 hrs. at 800°C, the surface features are partly obscured by the thick oxide layer which formed.

Auger electron spectroscopy is used to characterize the oxide layer profile of Vitallium specimens which had been oxidized in air or a partial vacuum. Information regarding the depth profile of metal ions in the oxide layer is necessary for correlation with AES analysis of the glass-metal interface after the oxide layer is dissolved in the glass. A description of the AES technique including operating conditions and sample preparation is given in Chapter III.

The variation of chromium, cobalt, and oxygen with time of ion milling is shown in Fig. 8 for a Vitallium specimen which had been oxidized in air at 600°C for 10 min. A typical peak for each element of interest (see Fig. 1) was selected, measured, and plotted versus time of ion milling. Tables 5 and 6 list the measured and normalized peak heights for an air-oxidized and a partial vacuum-oxidized specimen, respectively. The ion milling of each specimen was continued until the unoxidized alloy was reached. The depth of each data point from the surface can be estimated by using 50 Å/min. as the rate of ion milling. Based on this milling rate, the thickness of the oxide layer on the air-oxidized specimen is about 0.35 µm.

A comparison of the AES analysis of a Vitallium specimen oxidized in air at 600°C for 10 min. to that of a similar specimen oxidized in a partial vacuum (about 1 torr pressure) for the same time and temperature is given in Fig. 9. The following observations can be made from the normalized data:

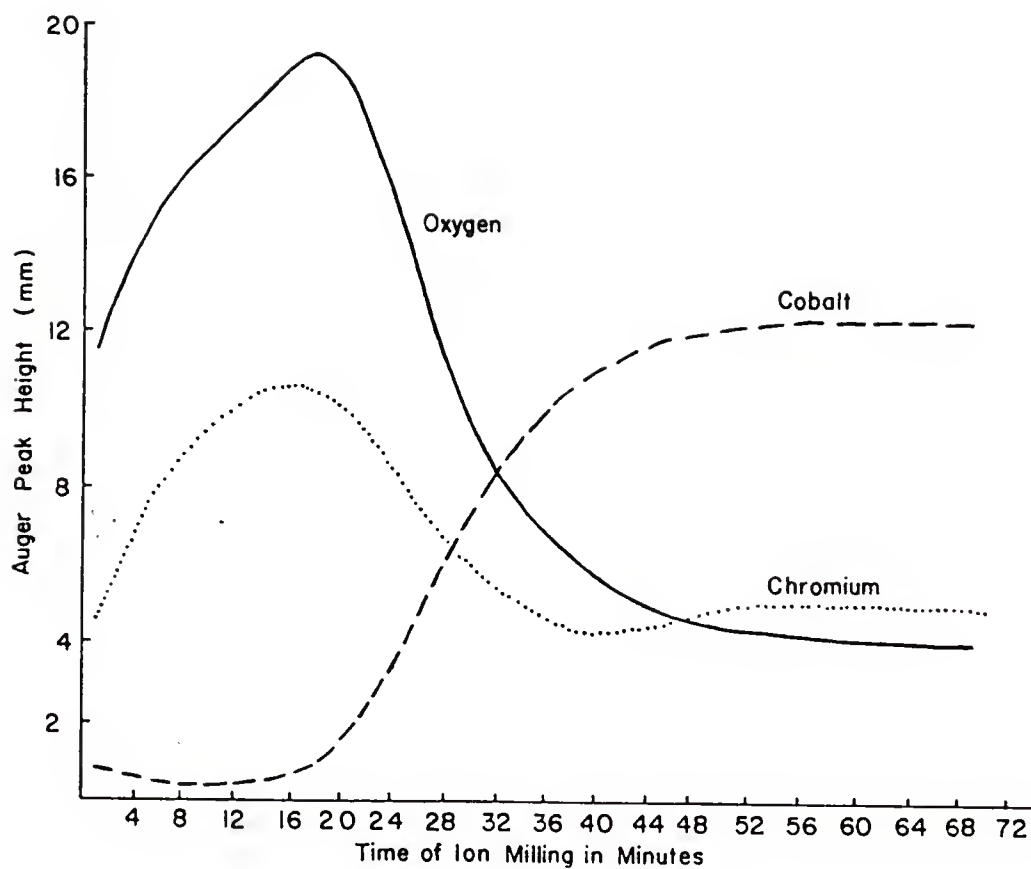


Figure 8. Auger electron spectrographic analysis of the surface of a Vitallium specimen oxidized at 650°C for 10 min. in air.

Table 5
Auger Electron Spectroscopy of Vitallium
Specimen Oxidized in Air

Time	Peak Heights in mm, Time of Argon Milling in Min.			
	O	Cr	Co	Cr (Normalized)
0-2	11.4	1.35	6.75	4.59
3.4-6.1	15.6	2.3	0.6	7.83
8.4-10.4	16.85	2.9	0.5	9.86
10.7-13.3	17.2	3.2	0.25	10.89
16.2-18.4	19.2	1.6	0.7	10.72
18.7-20.4	17.9	3.1	1.4	10.54
20.8-22.2	16.5	2.9	2.4	9.86
23.0-24.8	15.3	2.55	3.6	8.67
25.5-27.0	12.9	2.2	5.3	7.48
27.5-29.0	11.0	1.85	6.5	6.29
29.7-31.3	9.2	1.75	7.85	5.95
32.5-34.0	7.9	1.6	9.2	5.44
34.5-36.0	7.1	1.5	9.9	5.1
39.0-41.0	5.8	1.3	11.2	4.42
45.5-47.0	5.2	1.4	11.95	4.76
50.0-51.5	4.8	1.5	12.3	5.1
56.5-58.0	4.35	1.5	12.6	5.1
68.0-69.5	4.2	1.6	12.7	5.44

Table 6
Auger Electron Spectroscopy of Vitallium Specimen
Oxidized in a Partial Vacuum

Time	Peak Height in mm, Time of Ar Milling in Min.					
	0	Cr	Co	Normalized		
				Cr	Co	0
0-2.8	14.1	3.1	0.3	10.23	0.35	16.67
3.6-5.9	15.6	3.3	0.3	10.89	0.35	18.43
6.5-9.0	16.7	3.2	0.6	10.56	0.71	19.72
9.5-11.5	15.6	2.8	1.7	9.24	2.01	18.43
14.6-16.0	11.7	2.1	4.3	6.93	5.08	13.82
16.5-18.0	6.6	1.4	7.95	4.62	9.39	7.80
18.2-19.6	4.05	1.2	9.85	4.00	11.64	4.78
20.5-22.0	3.15	1.1	10.65	3.63	12.58	3.72
23.0-24.5	2.9	1.15	10.8	3.79	12.76	3.43
27.5-29.0	2.6	1.2	11.0	3.96	12.99	3.07
38.0-39.5	2.25	1.45	10.9	4.78	12.88	2.66
44.0-45.5	2.35	1.65	10.75	5.44	12.70	2.78

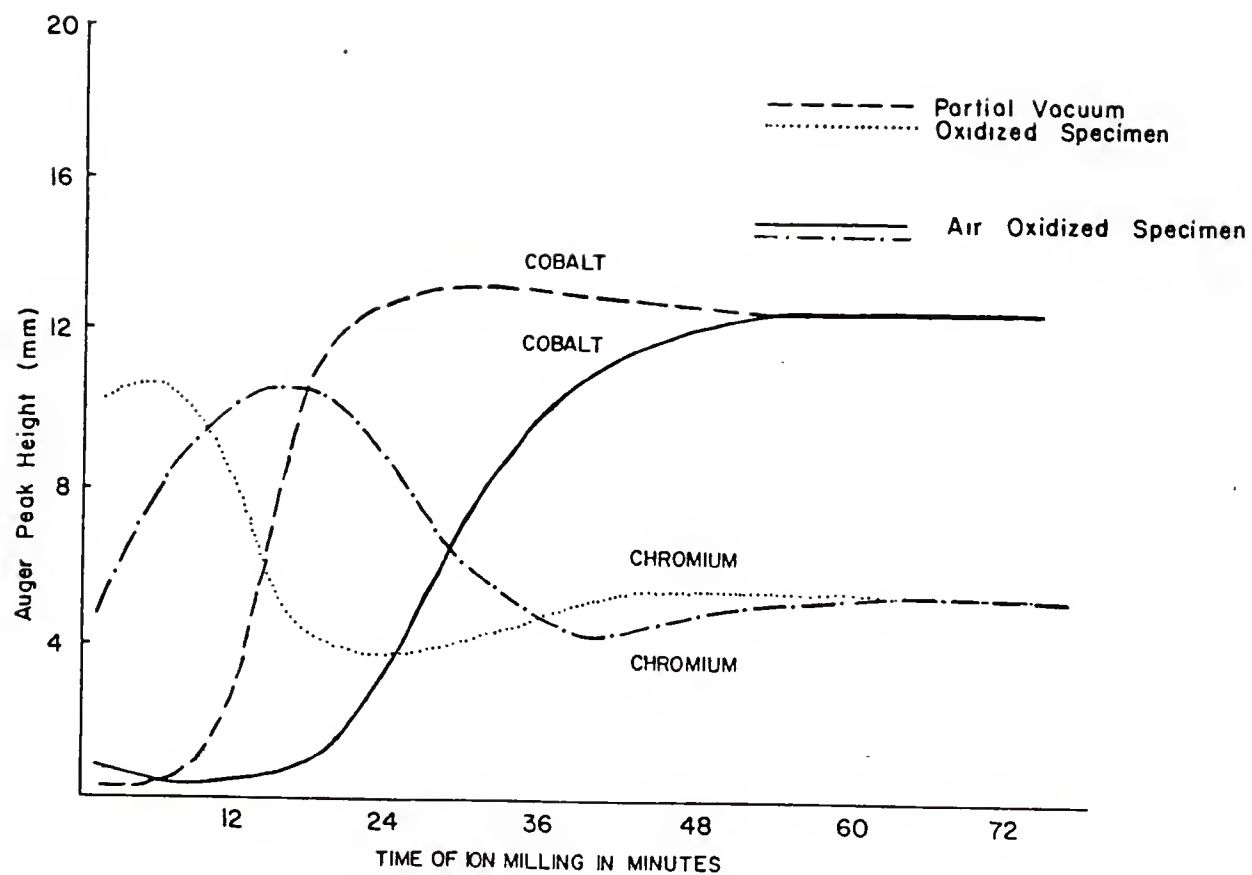


Figure 9. Auger electron spectrographic analyses of the surfaces of Vitallium specimens oxidized at 650°C for 10 min. 1) oxidized in air, and 2) oxidized in a partial vacuum (1 torr).

1. The maximum chromium peaks for both specimens are approximately equal and significantly greater than the chromium level of the unoxidized alloy. This indicates that a healing Cr_2O_3 layer formed for both specimens, the only difference being the distance from the surface at which this layer is located. The Cr_2O_3 layer is much closer to the surface for the specimen oxidized in a partial vacuum (5 min. milling or $\sim 250 \text{ \AA}$ vs. 15 min. milling or $\sim 750 \text{ \AA}$), indicating that this layer formed earlier in the oxidation process than the case of the air-oxidized sample.
2. The relative amount of cobalt at the surface is much higher for the specimen oxidized in air (16% vs. 3% relative to the chromium level). This indicates that more CoO had a chance to form at the surface of the air-oxidized specimen before the healing Cr_2O_3 layer was formed.
3. There is a chromium-depleted region for both specimens between the chromium-rich oxide layer and the bulk metal.
4. The thickness of the oxidized layer is greater for the specimen oxidized in air as more oxygen was able to diffuse into the specimen during the 10 min. firing time. It took about 70 min. of ion milling to reach bulk metal in the specimen oxidized in air as compared to only 45 min. for the other.

These observations concur with results from the literature which show that a chromium-rich oxide is formed during the oxidation of cobalt-chromium alloys. However, most of the literature studies are concerned with the oxidation of cobalt-chromium alloys at temperatures in excess of 1000°C for periods of several hours (e.g., conditions which are likely to be encountered in jet engines). Under these conditions thick oxide layers are formed (on the order of $100 \text{ }\mu\text{m}$ or more) and problems such as spalling of the oxide layer during cooling are much more severe. A thin oxide layer (less than $2 \text{ }\mu\text{m}$) such as is required for the immersion coating of Vitallium with Bioglass is more likely to be tightly bonded to the metal than a thick layer because

- 1) the thermal mismatch between oxide and metal is more easily relieved

during cooling, and 2) there is minimal void formation at the metal-metal oxide surface. It remains to be determined whether special techniques to improve the bonding of the thin layer of oxide to the bulk Vitallium alloy are effective in increasing the strength of the Bioglass-Vitallium bond.

CHAPTER VI
EFFECT OF COATING PROCESS VARIABLES ON
GLASS-METAL BOND STRENGTH

Immersion Process Variables

One of the objectives of this research program was to determine what effect such factors as surface roughness have on the strength of the bond formed between a glass and metal. To accomplish this objective, the processing variables which are important in the immersion technique (and similar to those of other coating methods) were optimized so that maximum bond strength of the coated test specimens was obtained. A secondary result of this optimization study was the corresponding increase in the coating adherence and integrity of Bioglass-Vitallium implants.

The most important coating process variables are:

1. Pre-immersion cleaning cycle for metal substrate.
2. Surface condition of metal.
3. Temperature and time of oxidation of metal.
4. Oxygen pressure during metal oxide layer formation.
5. Temperature of molten glass and time of immersion.
6. Post-immersion annealing cycle.

Each of the above will be discussed in regard to its effect on the glass metal bond strength.

Data obtained from the push thru shear test were used to evaluate the effect of each of the immersion process variables on the strength of the Bioglass-Vitallium bond. Means and standard deviations were calculated using the bond strength results from each test, but a more sophisticated statistical analysis was needed in several cases to determine if the observed differences between the means were significant. For each test group (e.g., cleaning agents), an analysis of variance gave an F value and a probability factor ($PR > F$) which were used to indicate whether there was a significant difference between any of the means within the group. A high F value and a low $PR > F$ factor is an indication that at least one of the means is significantly different from the others. On the other hand, a low F value and a high probability factor indicate that there is no difference between any of the means. Duncan's Multiple Range Test was used to define which means were significantly different from the others in test groups where the F value was sufficiently large. In the tables of results given in this chapter, the means are ranked in order of bond strength and those within a test group which are not significantly different will be bracketed together using the same letter (A, B, etc.).

Cleaning Cycle for Metal Substrate

The pre-immersion cleaning cycle used for the Vitallium test specimens was found to be one of the least important of the variables listed above. Surface cleanliness is usually of primary importance when coating one material with another, as impurities on the substrate

surface often cause a reduction of wetting and subsequent decrease of adherence. It was expected that at least some of the organic matter on the metal surface would be volatilized during the oxidation/preheat operation. A test was set up to determine the effectiveness of chemically cleaning the metal surface prior to oxidation. The following cleaning agents were used for ultrasonically cleaning the Vitallium test rods:

1. acetone
2. trichloroethylene
3. No-San* caustic solution used to clean dental crowns
4. Alconox** detergent followed by acetone

All these agents were judged to be satisfactory for cleaning Vitallium (Table 7), and there was not a significant difference between any of the mean shear strength values for this test group. Test pieces which were deliberately handled and oxidized without cleaning showed faint prints in the thin oxide coating, emphasizing the need for a cleaning cycle of some kind. Acetone was selected as the cleaning agent for use in the remainder of the program, due to its observed effectiveness in removing organic contamination and its less toxic nature as compared to trichloroethylene.

Surface Roughness of Metal

The nature of the surface of the metal substrate before oxidation has been shown to have an important effect on glass-metal bond strength

*Trio-Dent, Inc., Union, NJ

**Alconox, Inc., New York, NY

Table 7
Effect of Cleaning Agent on Bond Strength

F = 0.33; PR > F = 0.8053				
Agent	N	Std. Dev.	Mean (Kg/cm ²)	
Trichloroethylene	8	6.6	65.04	A
Acetone	8	4.3	64.53	A
Alconox/Acetone	6	3.1	64.00	A
No-San Caustic	5	4.2	62.04	A

in many cases. It has been shown by a number of researchers³³⁻³⁵ that increased surface roughness is beneficial to bond strength because of added mechanical interlocking of the glass coating. Others have found that increased surface roughness decreases bond strength if 1) the glass is too viscous to penetrate into the small surface cavities,⁷⁵ or 2) the surface is so rough that the sharp reentrant angles between glass and metal increase the stress concentration at the bond.⁵⁸

To determine the effect of surface roughness on shear strength and coating behavior, as-received cast Vitallium rods were polished with SiC paper, roughened by grit blasting, or electropolished in acid to obtain test surfaces of uniform roughness.

- a) Silicon carbide paper with a grit size of 180 was used to obtain a metal surface characterized by coarse, parallel ridges.
- b) A mixture of 50% Al_2O_3 particles and 50% glass beads under a pressure of 90 psi was used to grit blast selected Vitallium test specimens to obtain a uniformly roughened surface.
- c) A solution of perchloric acid was used to electropolish the test specimens at 65 amps for 60 sec.

Typical microstructures of SiC-polished grit blasted, and electropolished Vitallium specimens showing various degrees of surface roughness are shown in Fig. 10.

A shear strength test of coated rods in which the surfaces were conditioned in the three ways mentioned above was completed prior to the main study of the immersion process. Results from Table 8 show that the grit blasted and SiC polished specimens had a higher shear strength than electropolished specimens. However, all of the specimens

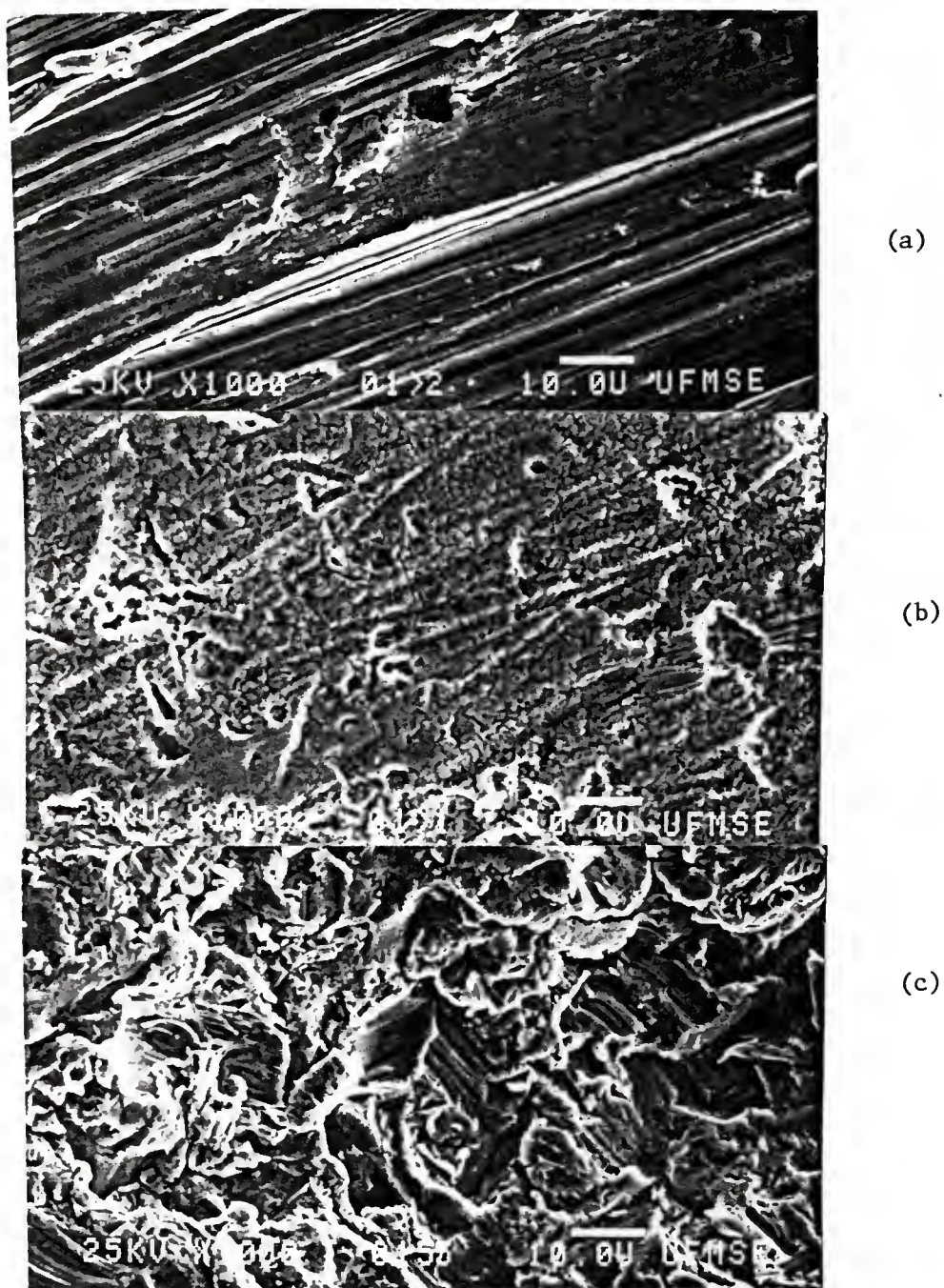


Figure 10. Scanning electron micrographs (1000X) of Vitallium surfaces roughened by various techniques:

- (a) SiC
- (b) Electropolished
- (c) Grit blasted

Table 8
Effect of Surface Roughness on Bond Strength

F = 5.06; PR > F = 0.0173				
Roughening Method	N	Std. Dev.	Mean (Kg/cm ²)	
Grit Blast	8	2.7	64.14	A
Silicon Carbide	7	6.0	62.04	A
Electropolish	7	6.7	55.43	B

in this test had higher shear strengths than the cast rods which had been coated in the as-received condition, indicating that removal of the outer layer of the cast metal has an important effect on glass-metal adherence.

From these results it appears that some degree of surface roughness is beneficial to increasing glass-metal adherence in the Bioglass-Vitallium system. The grit blasting method of surface roughening was selected over polishing by hand using SiC paper because of the ease and quickness of this technique and the more uniform nature of the roughened surfaces. Except for a few special test specimen, the remaining optimization of the immersion process was accomplished with the use of grit blasting as the surface roughening technique.

Temperature and Time of Oxidation of Metal

Two of the most important variables in the establishment of good glass-metal adherence are the temperature and time of the oxidation of the metal substrate prior to immersion in molten glass. These factors are responsible for the thickness of the oxide layer formed during oxidation of the metal at a given oxygen pressure. Oxide layer thickness is of critical importance, as an excessively thick oxide is usually weak and failure may occur within the oxide layer itself or between the metal and oxide. On the other hand, an oxide layer which is too thin may be completely dissolved by the glass, causing loss of saturation of metal oxide at the glass-metal interface.

To determine the effect of time and temperature of oxidation on shear strength, approximately 150 Vitallium rods oxidized at nineteen different time-temperature combinations (5-15 min., 350-800°C) were coated and then prepared and tested according to the procedures described in Chapter IV. All other process variables remained constant:

- a) cleaning cycle--acetone (ultrasonic)
- b) surface condition--grit blasted
- c) oxygen pressuring during oxidation--atmospheric
- d) molten glass temperature--1330°C to 1340°C
- e) immersion time--3 sec.
- f) annealing cycle--500°C for 4 hrs., furnace cool

The shear strength results of this controlled test are given in Table 9. The optimum time-temperature oxidation cycle could not be established from this test because of the scatter in the test data. The eight cycles with the best shear strength means were grouped together as being statistically the same. Any of the time-temperature combinations from this group should give acceptable results.

A plot of the shear strength vs. time of oxidation is shown in Fig. 11 for some of the oxidation temperatures used in this test. In general, for a given temperature in the range of 500°C to 650°C, the shear strength increases with increasing time of oxidation to a certain point then decreases. For a temperature of 800°C, shear strength values decrease as oxidation time is increased over 5 min. A 350°C oxidation temperature gives low bond strengths regardless of oxidation time.

These results show that an optimum time of oxidation occurs for each temperature, thus indicating that a certain thickness of an oxide

Table 9

Effect of Oxidation Time and Temperature on Bond Strength

F = 15.97; PR > F = 0.0001				
Oxidation Cycle	N	Std. Dev.	Mean (Kg/cm ²)	
500°C - 15 Min.	7	3.6	64.76	A
575°C - 10 Min.	4	3.6	64.33	A
620°C - 10 Min.	4	2.6	63.13	A
620°C - 15 Min.	4	4.1	63.00	A
650°C - 10 Min.	7	4.3	62.90	A
540°C - 15 Min.	4	5.9	62.35	A
575°C - 15 Min.	4	2.7	61.38	A
500°C - 10 Min.	4	3.7	59.10	A
650°C - 5 Min.	7	2.2	55.34	B
620°C - 5 Min.	3	9.1	55.27	B
540°C - 10 Min.	4	4.7	54.98	B
650°C - 15 Min.	7	5.3	49.09	B
575°C - 5 Min.	3	0.9	49.00	B
540°C - 5 Min.	5	5.0	48.84	B
800°C - 5 Min.	7	8.3	47.26	B
500°C - 5 Min.	4	4.7	44.50	C
800°C - 10 Min.	5	7.9	38.06	C
800°C - 15 Min.	6	5.1	33.58	D
350°C - 10 Min.	3	5.7	26.37	E

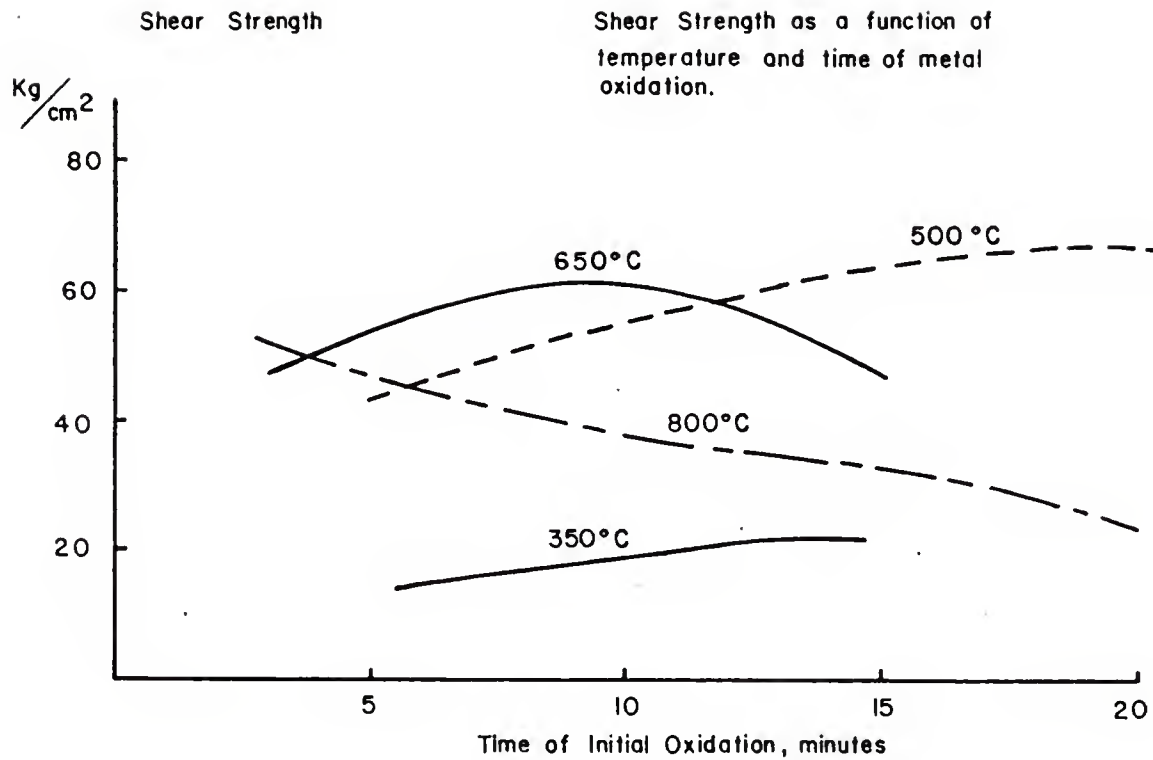


Figure 11. Bioglass-Vitallium bond strength as a function of time and temperature of oxidation.

layer gives maximum bond strength. An oxidation temperature in the range of 500°C to 650°C is the most suitable for Vitallium, with oxidation times being 8 to 15 min. depending on the temperature. The use of a time-temperature cycle in this range gives about 40% better shear strength test results than the previously-used standard oxidation cycle of 800°C for 10 min. The use of 800°C as an oxidation temperature requires very short times which tends to produce irregular oxidation of the metal substrate. In addition, temperatures over 650°C cannot be used for either cast or wrought Vitallium specimens if the desired mechanical properties are to be maintained. Temperatures below 500°C give low shear strength values due to insufficient oxide layer formation and excessive temperature mismatch between molten glass and preheated substrate causing the glass to chill before it can completely wet the substrate.

Temperature of Molten Glass and Time of Immersion

The temperature of the molten glass affects both its fluidity and the rate at which the metal oxide layer is dissolved. Higher glass temperatures cause an oxide layer of a given thickness to be dissolved in a shorter time, thus requiring a change in other process variables to assure that some oxide remains on the metal. The most important effect of glass temperature on the coating process, however, is on the thickness of the glass coating which remains on the metal substrate after immersion. The glass temperature must be maintained within a certain range to 1) avoid an excessively thick Bioglass coating

(i.e., greater than 2 mm) on the Vitallium substrate and 2) be below a temperature at which significant vaporization of Na_2O from the glass melt can occur. The two constraints put the acceptable glass temperature in the range of 1300°C to 1360°C .

The results of a study designed to show the effect of glass temperature on shear strength are given in Table 10. There was a range of coating thickness (0.8 mm to 1.9 mm) observed for rods immersed in glass at temperatures from 1300°C to 1350°C , but there was no significant difference in the average shear strength of the coated specimens.

The time of immersion has been found to have a greater effect on bond strength than the temperature of immersion. A test was designed to determine whether longer immersion times could cause increased bond strength by the removal of part of the oxide layer on metal substrates which had been excessively oxidized. The coating of Vitallium rods by immersion in Bioglass for 15 sec. and 30 sec. as compared to the normal 3 sec. immersion was accomplished on a number of specimens. Shear strength results (Table 11) show a slight but significant decrease in strength with increasing time of immersion, perhaps as a result of the increase in porosity observed at the glass-metal interface. Also, a longer immersion time is undesirable because of the alteration of the metal structure caused by subjecting the substrate to the extremely high temperature of the molten glass (about 1350°C).

Post-Immersion Annealing Cycle

An annealing cycle is necessary to relieve the stresses in the glass coating prior to cooling to room temperature. The glass layer

Table 10
Effect of Glass Temperature on Bond Strength

F = 0.19; PR < F = 0.0990				
Glass Temperature	N	Std. Dev.	Mean (Kg/cm ²)	
1320°C	6	4.5	64.60	A
1335°C	7	2.6	63.56	A
1350°C	6	4.7	62.57	A
1330°C	7	4.3	62.16	A

Table 11
Effect of Immersion Time on Bond Strength

F = 13.11; PR > F = 0.0002				
Immersion Time	N	Std. Dev.	Mean (Kg/cm ²)	
3 Sec.	8	5.0	64.60	A
15 Sec.	8	4.1	58.14	B
30 Sec.	8	4.5	51.03	C

at the interface is under especially high stress during cooling because of the thermal expansion mismatch with the metal substrate. A study showed that an annealing cycle is necessary for good glass-metal adherence, but there is a wide range of annealing times and temperatures which gives acceptable results (Table 12). There was no significant difference in the shear strength of coated specimens annealed at temperatures of 450°C to 600°C and for times of 2 to 6 hrs. Based on these results, a cycle of 4 hrs. at 500°C followed by furnace cooling was established as the standard annealing cycle for the remainder of the immersion coating program.

Oxygen Pressure During Oxidation

Reduced oxygen pressures for the oxidation of a metal substrate have been shown to increase metal oxide-to-metal adherence, as discussed in Chapter V. An AES analysis of the oxide profiles of Vitallium specimens oxidized in air (Fig. 8) and in a partial vacuum showed similar cobalt and chromium profiles for both specimens. The thickness of the oxidation layer formed in air, however, is greater than that formed in a partial vacuum under the same time/temperature conditions (Fig. 9).

A study was conducted to determine if the formation of an oxide layer in a low-oxygen environment leads to increased glass-metal adherence. Air-oxidized specimens were processed in the usual manner; partial-vacuum oxidized specimens were taken from the Jelcraft furnace (see Chapter III), cooled to room temperature, then preheated at 650°C for 2 min. prior to immersion. Results show a dramatic improvement in

Table 12
Effect of Annealing Cycle on Bond Strength

F = 0.19; PR > F = 0.9425				
Annealing Cycle	N	Std. Dev.	Mean (Kg/cm ²)	
4 Hr. - 500°C	6	6.1	63.67	A
6 Hr. - 600°C	5	3.2	63.30	A
2 Hr. - 450°C	6	6.9	63.07	A
2 Hr. - 600°C	5	7.1	62.04	A
6 Hr. - 450°C	7	6.5	60.63	A

bond strength of specimens oxidized at 800°C for 10 min. at 1 torr pressure as compared to specimens oxidized in air at the same time and temperature (Table 13). However, shear strength results of both groups of specimens oxidized at 650°C for 10 min. were similar, and at 500°C for 10 min. the average bond strength of the specimens oxidized in air was significantly higher. These results show that the use of a partial vacuum is effective in increasing shear strength only for time/temperature oxidation conditions which would give an excessively thick oxide layer if oxidation occurred in air. This observation reemphasizes the importance of the formation of an oxide layer of proper thickness on the metal substrate, and indicates that oxide thickness is of greater importance than increased metal oxide-metal adherence if sufficient adherence is already present.

Degassing of Metal Substrate

The evolution of gasses during the coating of a metal with glass is also an important factor which must be considered in any attempt to optimize a particular coating process. Degassing of the metal substrate in the immersion process proved to be difficult and the optimization program was carried out without inclusion of a specific degassing step. The presence of bubbles at the glass-metal interface ranging from small to microscopic sizes was noted for every Vitallium specimen coated by the immersion process. The exact effect of porosity at the glass-metal interface is unknown, but would at least be a reduction in bonding strength equal to the contact area which is lost. Porosity in

Table 13
Effect of Oxidation Pressure on Bond Strength

F = 11.89; PR < F = .0065				
Cycle (10 Min.)	N	Std. Dev.	Mean (kg/cm ²)	
650°C - Air	11	4.1	60.64	A
800°C - Vacuum	5	2.9	58.03	A
500°C - Air	7	5.3	56.59	A
650°C - Vacuum	6	3.0	55.22	A
500°C - Vacuum	6	4.3	43.23	B
800°C - Air	8	4.9	39.91	B

glass and ceramic materials has been shown to change the thermal expansion coefficient, heat capacity, and lower the tensile and impact strengths. Bubbles at the glass-metal interface may account for the wide scatter of values reported in most bond strength tests.

Metal outgassing is a common occurrence in most metal coating operations which occur at elevated temperatures. In glass-to-metal sealing, degassing of the metal substrate in a vacuum is sometime carried out prior to sealing (usually for the removal of hydrogen). There is also a degassing step in the preparation of dental crowns which was originally intended to remove organic material deposited on the surface of the metal by the rubber polishing discs. The metal is typically taken to just over the subsequent firing temperature then coated to room temperature before coating with porcelain. In a study on gold alloys, O'Brien⁷⁶ found that no gas was given off from the metal during this operation if the metal had first been properly cleaned; however, specimens handled before heating showed significant gas evolution. If gas is picked up by the metal during melting, degassing may have a significant effect on the bond strength. McLean and Sced⁷⁷ found that gold alloys which were subjected to an outgassing treatment of 900°C for 2 hrs. at 10^{-3} torr had almost 50% better bond strength after coating with porcelain than similar specimens which were not outgassed. The increase in strength was attributed to the removal of hydrogen, as the metal had been induction melted in a hydrogen atmosphere. The low bond strength of the coated metal which was not outgassed was attributed to the porosity observed at the glass-metal interface.

Extensive gas evolution has been observed during the firing of porcelain coatings on steel. Lucian and Kautz⁷⁸ identified these gases as H_2 , H_2O , CO , CO_2 , and N_2 . Porosity in the glass in the later stages of firing has been attributed to metal outgassing, and Andrews⁷⁹ found that gas may also become trapped between the steel substrate and the porcelain coating. Refiring the metal substrate or outgassing prior to coating has been shown to be effective in reducing the gas evolution from the metal. Most of the porosity at the porcelain-steel interface comes from the reaction of metal oxides in the gas with carbon in the steel causing the formation of CO_2 . Some of the gas formed escapes as the ground coat is being fired. In one-coat enameling, however, very low carbon steel (less than 0.005%) must be used in order to prevent the formation of porosity and other defects.⁸⁰

The evolution of gases during the coating of a metal by a glass occurs primarily from the following sources: 1) volatilization of hydrocarbon compounds on the metal surface, 2) diffusion of hydrogen and nitrogen from the internal metal structure, and 3) oxidation of carbon in the metal to form CO and CO_2 . In order to determine if the occurrence of porosity at the Bioglass-Vitallium interface could be controlled, a test was initiated to show which of these three factors was primarily responsible for the observed bubbles. The following variables were studied using 6 mm diameter cast Vitallium rods:

- a) Cleaning cycle - for grit blasted rods, cleaned ultrasonically
 - 1) acetone
 - 2) trichloroethylene
 - 3) caustic solution
 - 4) detergent, acetone

b) Surface condition of metal

- | | |
|--------------------|------------------|
| 1) grit blasted | 3) 180 SiC paper |
| 2) electropolished | 4) as-received |

c) Heat or vacuum treatment

- 1) heated to 800°C for 3 hrs. in air
- 2) heated to 650°C for 10 min. in a partial vacuum (1 torr)
- 3) outgassed at 650°C for 1 hr. at 10^{-5} torr
- 4) outgassed at 900°C for 1 hr. at 10^{-5} torr

The specimens cleaned ultrasonically in the four cleaning agents were oxidized at 650°C for 10 min. before being immersed in Bioglass. A separate specimen which was purposely contaminated (finger printed) was oxidized and coated at the same time without having been cleaned. Virtual observation of the glass-metal interfacial region of each specimen revealed that the number and size of bubbles present was approximately the same regardless of cleaning method. This shows that the oxidation heat treatment removes much of the organic debris on the metal surface; thus the cleaning cycle is not a factor which can be used to control the presence of bubbles at the glass-metal interface. Uncleaned and contaminated surfaces were found to cause a lower glass-metal bond strength, but this was due to poor wetting of the glass and not to increased porosity at the interface.

Vitallium rods with the various surface conditions listed above were oxidized at 650°C for 10 min. before immersion in Bioglass to determine the influence (if any) of the surface condition of the metal

substrate on gas evolution during coating. A change in outgassing behavior might be the result of the following factors:

- 1) A surface roughened by grit blasting may include more trapped gases which are subsequently released during firing.
- 2) A grit blasted specimen has more than twice the surface area of an electropolished specimen. Thus more metal is exposed to molten glass, and more reactions which liberate gas may occur.
- 3) As-received cast metal may have surface layers with increased work or non-uniform composition due to segregation effects during casting. In a steel casting, for example, the outer layer which typically contains higher carbon must be removed by grit blasting or pickling to avoid excessive gas evolution during porcelain enameling.

Observation of the coated specimens showed no difference in the extent of porosity at the glass-metal interface. Grit blasting had been shown (by AES) to increase the thickness of the oxide layer formed on Vitallium, but neither the increased surface work nor surface area had an apparent effect on the occurrence of glass-metal interfacial porosity.

A vacuum heat treatment is usually the most effective means of degassing a metal substrate. Most metals containing hydrogen and nitrogen can be degassed in a high vacuum, but the decomposition pressures of most oxides and carbides are so low that removal of these elements under attainable temperatures and vacuums is not possible.⁸¹ A high vacuum (10^{-5} torr) and a partial vacuum (1 torr) were used to heat treat the Vitallium specimens at the maximum acceptable temperature of 650°C. For comparison purposes, several specimens were also degassed at 900°C and 10^{-5} torr. Other cast Vitallium specimens were fired at 800°C for

3 hrs. in air to effect massive carbide precipitation in an attempt to decrease the evolution of CO and CO₂ from the metal.

Examination of the glass-metal interfaces of each specimen after immersion coating with Bioglass revealed the presence of approximately equal quantities of bubbles in each. These test results show that carbon from the metal in combination with oxygen from the glass is the likely source of the gas evolved during immersion, since any hydrogen or nitrogen in the Vitallium would have been removed by the 900°C, 10⁻⁵ torr heat treatment. The 800°C, 3 hr. heat treatment in air was unsuccessful in preventing the glass-carbon reaction.

In summary, it was determined that the cleaning cycle, surface condition of metal, and various degassing treatments have little observed effect on the occurrence of porosity at the glass-metal interface. The conclusion is that the gas liberated during immersion is the result of a reaction of an oxide in the glass with a component of the metal alloy. This is a common occurrence in the enameling of porcelain to steel, for example, as CO and CO₂ are formed due to the reaction of carbon in the steel with an oxide in the glass. From a table of standard free energies of formation of metal oxides as a function of temperature,⁴² it can be noted that at a temperature of 750°C or higher carbon can reduce P₂O₃ and be itself oxidized to CO or CO₂. Sodium dioxide can also be reduced by carbon at temperatures below 1000°C, and Na (boiling point - 892°C) is more volatile than P. At the high temperature of the molten glass (i.e., 1350°C) there is a higher thermodynamic driving force for these and similar reactions

to occur at the glass-metal interface. The gas which is produced stays as porosity at the interface because the viscosity of the molten Bioglass is too high to allow movement of bubbles to the surface.

The cast Vitallium rods used for the optimization of the immersion coating process contain 0.25% carbon, a level which is much higher than that which can be tolerated for steel which is to be used for porcelain enameling. Use of the immersion process puts much greater demands on the metal substrate because: 1) a higher maximum temperature (1350°C compared to 900°C for porcelain-steel enameling) is used, causing more reaction of carbon in the metal with oxides in the glass, and 2) the frit enameling method allows some gas to escape before the frit particles fuse together, while the quick immersion technique traps the gas at the interface because of the high viscosity of the glass. In spite of its disadvantages, the immersion process is still the coating method of choice for the Bioglass-Vitallium system because: 1) the flame spray coating process causes even more voids at the glass-metal interface, 2) the frit-enameling method requires higher temperatures for times which would cause a decrease in the desired properties of the Vitallium substrates. As degassing of the Vitallium was shown to be ineffective using available techniques and equipment, the optimization of the immersion process was carried out without including a degassing operation.

CHAPTER VII
GLASS COMPOSITIONAL AND COATING MODIFICATIONS

Enameling and Double Coating of Vitallium with Bioglass

As discussed in Chapter II, frit enameling is the most commonly used technique for coating a metal substrate with glass. It is not the preferred coating method for the Bioglass-Vitallium system, however, because of the excessive metal ion diffusion into the Bioglass and the loss of mechanical properties of the Vitallium substrate during the coating operation. In this study, a number of Vitallium specimens were coated with Bioglass frit in order that a direct comparison could be made between the bond strengths and interfacial microstructures of specimens coated by this technique and those coated by the immersion method.

For enameling purposes, 52S4.6 Bioglass pieces were ground (dry) in an alumina ball mill until a particle size was reached which would pass through a 400 mesh screen ($38\text{ }\mu\text{m}$ or less). The ground frit was added to a vehicle of 70% toluene and 30% acetone which aided in the transfer and coating of the frit particles onto the metal substrate. Vitallium rods were dipped into the frit solution a total of three times, with the coating allowed to dry for several minutes before the next layer was applied. The coated specimens were heated at a temperature of 500°C to allow the organic residues from the vehicle to

be extinguished. The frit-coated substrates were fired at 1100°C for 5 min. to allow the Bioglass to fuse so that a smooth coating was formed on the Vitallium. The coated specimens were annealed at 500°C for 4 hrs. and furnace cooled to room temperature.

The glass coating thickness on Vitallium rods enameled by the above procedure was approximately 200 μm . The bond strength of these specimens could not be determined by the use of the push thru shear test because only a thin layer of glass was present on the metal. To facilitate the testing and evaluation of the glass-metal interface, thicker coatings of Bioglass were applied to the Vitallium substrates by a procedure similar to that used for the preparation of porcelain-veneered-to-metal dental crowns. Bioglass frit mixed with the toluene-acetone vehicle was applied in small increments to the Vitallium substrate by the use of a brush. Tissue paper was used to wick the excess vehicle from each increment of frit as it was added to the coating, thus condensing the frit particles so that increased packing density was obtained. The coated test specimens were fired at the same time and temperature as the specimens which had been coated by dipping in the frit solution.

The brush-application technique proved to be successful in increasing the coating thickness (to 1.2 mm), but full density of the glass coating was not obtained with the firing cycle used. During shear testing of these specimens, fracture occurred within the glass coating and not at the glass-metal interface. Examination of the fracture surface revealed extensive porosity throughout the glass coating. Increasing the firing temperature and time caused the glass

to flow off the substrate before a smooth coating was obtained. Firing in a partial vacuum may be necessary to get full density of glass coatings applied by this technique.

A double coating of Bioglass was applied to Vitallium in an attempt to overcome some of the disadvantages inherent in the fritting process and to produce specimens with thicker coating which could be evaluated by the push thru shear test. In this procedure a layer of Bioglass is applied by frit enameling; then the specimen is immersed in molten Bioglass to obtain the second, thicker coating. Some advantages of double coating are: 1) there is no metal ion migration through the outer coating to the Bioglass reaction surface, 2) the composition of the inner layer can be altered to enhance bonding to the metal substrate while the outer layer retains its bone-bonding ability, and 3) porosity at the glass-metal interface is likely to be reduced by first putting on a fritted layer of glass.

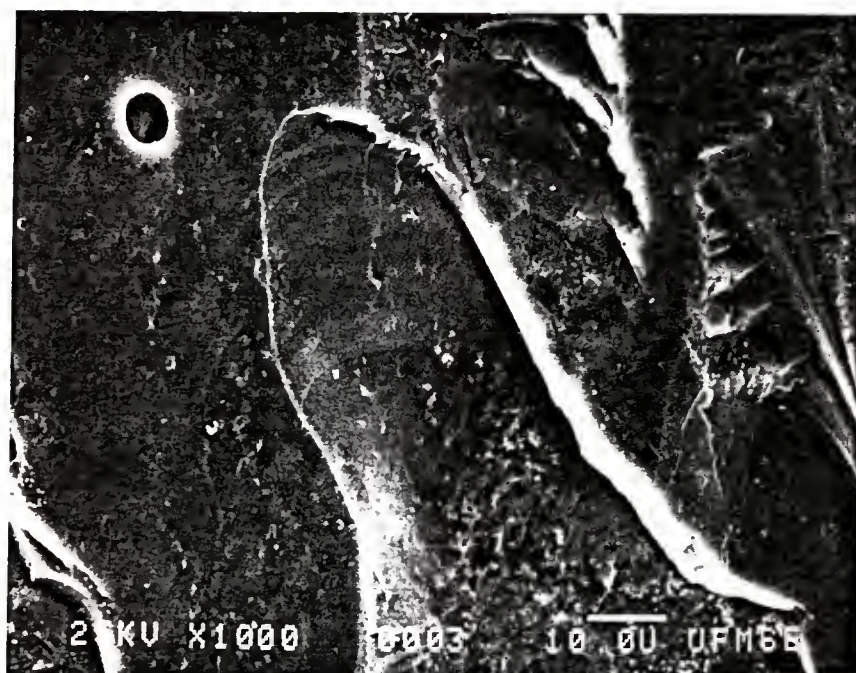
Average bond strength of double-coated specimens, however, was observed to be somewhat less than that for standard single-coated Bioglass-Vitallium specimens (Table 14). A very irregular fracture pattern was observed for the double coated specimens which were shear tested. Fracture predominately occurred between the two glass layers, but the fracture line would occasionally run through the inner (fritted) layer to the metal-glass interface. Scanning electron micrographs (Fig. 12) of the inter-glass fracture show the contrast between the smoother upper (immersion) and the grainier lower layer (frit enameled). An AES analysis showed high chromium at the surface of the inner layer where fracture occurred. An EMP analysis of a double coated specimen

Table 14
Bond Strengths of Various Special Test Specimens

Specimen	N	Mean Kg/cm ²	Std. Dev. Kg/cm ²
1. Thick Bioglass (Frit Enameled)	5	30.3	9.7
2. Double Coated (Frit + Immersion)	8	45.8	3.2
3. 52S4.6 Bioglass + 3% CuO	6	48.6	4.8
4. 45S5F Bioglass	6	64.1	3.1
5. Dental Porcelain-Vitallium	3	78.3	6.2



(a)



(b)

Figure 12. Scanning electron micrographs of a Vitallium specimen enameled with a layer of frit then immersed in molten Bioglass.

- (a) Fracture surface (100X)
- (b) Fracture surface showing distinct glass layers (1000X).

showed diffusion of both chromium and cobalt through the 100 μm thick inner glass layer, but no evidence that these elements had diffused past the junction of the two glass layers. There was no porosity visible at the glass-metal interface, but voids at the fracture surface indicated that gas had diffused to the interface between the two glass layers. These results will be further discussed in Chapter IX.

Addition of Adherence Oxides to Bioglass

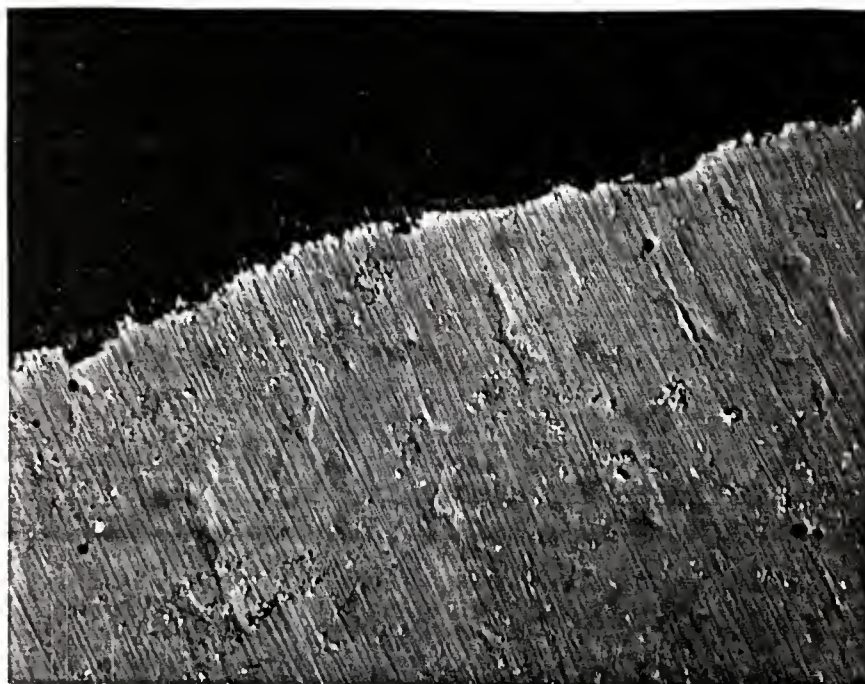
Oxides which have a high potential for reduction by the metal substrate during the coating operation can be added to the glass composition to increase glass-metal adherence. These oxides can increase the extent of interfacial roughness leading to enhanced mechanical interlocking between glass and metal. They can also function to maintain metal oxide saturation at the interface during firing and thus increase chemical bonding between glass and metal.

None of the component oxides in Bioglass has the potential for being reduced by the cobalt or molybdenum in the Vitallium substrate. Reduction of chromium by P_2O_5 or Na_2O is thermodynamically possible during the immersion process, but may not occur because of the short time at temperature. Copper oxide (CuO) was selected to be added to a special 52S4.6 Bioglass composition because copper has a lower negative free energy of oxide formation (Table 3) than all of the elements in the cobalt-base substrate alloy.

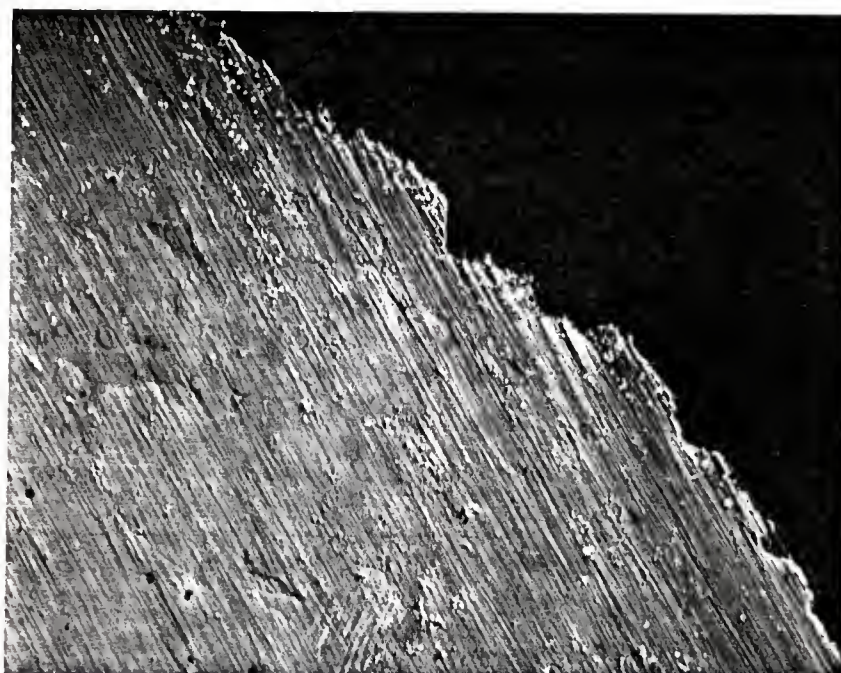
A 3% CuO (by weight) addition was made to the standard 52S4.6 Bioglass composition, with part of the batch fritted to be used in the frit enameling process and the other portion remelted in a platinum crucible to be used for immersion coating of Vitallium test specimens. The fritted Bioglass-3% CuO was coated onto test rods using a procedure similar to that described in the previous section; then a second coating (standard 52S4.6 Bioglass) was applied by immersion to produce a glass layer which was thick enough to enable the coated specimens to be shear tested.

The following results were obtained from the frit-enameling and immersion coating of standard Vitallium test rods using Bioglass which contain 3% CuO:

1. No increase in roughening of the glass-metal interface was accomplished during immersion of the Vitallium rods in Bioglass-3% CuO. The short immersion time (3 sec.) is insufficient to allow the proper oxidation/reduction reactions to occur.
2. The average shear strength of the specimens coated with Bioglass-3% CuO was not significantly different from that obtained for specimens coated with the standard Bioglass composition (Table 14).
3. An increase in roughness at the glass-metal interface was observed for the Bioglass-3% CuO frit-coated specimens. Figure 13a shows a typical interface of the frit-enameled 52S4.6 specimen fired at 1100°C for 5 min. Figure 13b is a similar specimen which was enameled with 52S4.6 Bioglass containing 3% CuO for the same time and temperature. In addition to the rougher surface of the Bioglass-3% CuO specimen, it can also be observed that this glass was more effective in dissolving the oxide layer during the coating process.
4. Certain small specks in the Bioglass-3% CuO layer may be metallic dendrites, but no positive identification has been made. Even if present these dendrites would have no effect on glass-metal adherence.



(a)



(b)

Figure 13. Scanning electron micrographs (400X) of Bioglass-Vitallium interfaces of frit-enameled specimens.

(a) 52S4.6 Bioglass

(b) 52S4.6 Bioglass + 3% CuO showing increased interfacial roughness.

5. The effect of the addition of CuO on Bioglass-Vitallium bond strength could not be determined because fracture occurred predominately between the glass layers. This fracture mode was also observed with the double coated specimens of the standard 52S4.6 composition, and the shear strength results from the two groups are similar (Table 14). Because of this irregular fracture pattern, the effect of CuO on shear strength (e.g., by increasing interfacial roughness) could not be determined by this body.

Bioglass Containing Fluorine

A special Bioglass containing fluorine (45S5F) was originally developed and used for the flame spray coating of metal because of the lower viscosity of this glass as compared to 52S4.6 for 45S5 Bioglass. The high fluidity of 45S5F has also been shown to be advantageous in the immersion coating of special implants with internal cavities and concave surfaces.

One reason for the inclusion of 45S5F in this study is that its coefficient of thermal expansion (α) differs from that of Vitallium by a greater amount than the α of 52S4.6 Bioglass (see Table 15). Thermal expansion measurements (accomplished by a procedure as described in Chapter III) showed that 45S5F has a somewhat lower α than 52S4.6 (by 2.8%), a result which is somewhat surprising because of the higher flux content of 45S5F.

A number of Vitallium rods were coated with 45S5F to determine the effect of a greater α mismatch on measured shear strength. The difference in α results in a higher stress level between glass and metal during cooling to room temperature after the coating operation. Although the exact effect of residual stress on bond strength is

Table 15
Thermal Expansion Coefficients of Bioglass and Vitallium

Specimen	α ($\times 10^6 / ^\circ\text{C}$)	Difference From Vitallium
Vitallium (Cast)	14.81	---
52S4.6 Bioglass	14.34	3.3%
52S4.6 Bioglass (70% Crystallized)	14.14	4.5%
45F5 Bioglass	13.91	6.1%

unknown, it is usually advisable to have as little interfacial mismatch as possible during the sealing or bonding of glass to metal. However, from Table 14 it can be seen that there was no significant difference in bond strength between the specimens coated with 45S5F glass and those coated with the standard 52S4.6 composition. This indicates that thermal expansion differences of this magnitude are not as important as other factors in regard to their effect on bond strength (as measured by this test).

Another justification for the inclusion of 45S5F in this study was to determine if the higher fluidity of this glass during immersion coating would allow the escape of gas bubbles from the glass-metal interface. A decrease in porosity at the interface of the coating and substrate would be expected to cause greater adherence between glass and metal. However, observation of 45S5F-coated specimens showed a level of interfacial porosity similar to that commonly observed for 45S4.6-coated Vitallium. The additional fluidity of the 45S5F is apparently not sufficient to allow the escape of gas from the interface.

Coating of Vitallium with Dental Porcelain

A number of Vitallium rod specimens were coated with dental porcelain and tested using the push thru shear test so a comparison could be made between the bond strengths of porcelain-Vitallium, Bioglass-Vitallium, and the literature values for porcelain bonded to Co-Cr dental alloys. This comparison is also useful in evaluating the relative severity of the push thru test as a means of measuring adherence.

A typical opaque dental porcelain used for bonding to metal contains SiO_2 (59%), Al_2O_3 (18%), K_2O (12%), Na_2O (5%), and small amounts of opacifiers such as SnO_2 .⁸² This composition has a lower flux content than 52S4.6 Bioglass, but the two materials have similar thermal expansion coefficients.

In coating the Vitallium test rods, porcelain powder* was added in small increments using a brush and the excess moisture from each addition was removed with a tissue. Vibration was employed to aid in condensing the porcelain so that denser packing of the particles was obtained. In order to produce a specimen which could be shear tested with a minimum of shaping, a stainless steel washer was placed 5 mm from one end of the Vitallium substrate rod. The washer was covered with platinum foil and fixed so that its surface was exactly perpendicular to the shaft. Porcelain was built up along a 15 mm length of unoxidized rod to a depth of about 0.8 mm. After drying the coating at the entrance to the Jelcraft furnace (see Chapter III), each test specimen was taken to a temperature of 950°C (at a rate of 55°C per min.) under a partial vacuum before furnace cooling. A second layer of more translucent porcelain was added in a similar manner but fired at a slightly lower temperature. The finished specimens were tested using the push thru shear test.

The average shear strength for porcelain-Vitallium specimens as given in Table 14 is higher than that for Bioglass-Vitallium, but a factor of 3 lower than some of the cobalt-chromium alloy-to-porcelain

*VMK 68, Vita Zahnfabrik, Sackingen, West Germany

bond strengths given in the literature. Two possible explanations for this difference are:

1. The push thru test is a more rigorous testing method than conventional adherence tests, as all the applied load is parallel to the glass-metal interface.
2. The Vitallium alloy in this study is used in dentistry primarily for partial denture castings, orthodontic wires, and implants and not as a metal to bond to porcelain. Cobalt-chromium alloys used for porcelain-veneered crowns typically contain additional elements such as silicon and aluminum which change the alloy oxidation characteristics and produce a stronger metal-metal oxide bond.

Fracture during shear testing of the porcelain-Vitallium occurred primarily at the metal-glass interface. A heavy, green oxide was observed on the porcelain fracture, while the surface of the glass metal was a shiny, silver color. This indicates that either fracture occurred between the metal and its oxide or that all the oxide was dissolved in the porcelain prior to fracture. Auger electron analysis of the porcelain-Vitallium fracture surfaces will be discussed in Chapter IX.

Effect of Bioglass Composition on Interfacial Porosity

The presence of pores or voids at the interface between Bioglass and Vitallium has been shown to have a detrimental effect on adherence. Previously attempts to minimize the formation of interfacial porosity by proper cleaning and degassing of the metal substrate were unsuccessful. Modifications of the Bioglass composition were made as another approach to determine the origin or source of this porosity.

As phosphorous pentoxide (P_2O_5) is the oxide in the glass which is most likely to be reduced by the metal substrate, a phosphorous-free Bioglass composition was formulated which included SiO_2 (55 wt %), Na_2O (22.5 wt %), and CaO (22.5 wt %). A variety of Vitallium specimens (e.g., grit blasted, electropolished, and vacuum oxidized) were coated with this glass following optimized immersion procedures. All of the coated specimens exhibited a typical amount of interfacial voids (i.e., an area fraction of .15 to .19), indicating that the presence or absence of P_2O_5 has little effect on the formation of porosity.

Another approach was to substitute an equal molar percentage of lithium oxide (Li_2O) for Na_2O , giving a glass with a composition of (by wt): 57.5% SiO_2 , 25.5% CaO , 12% Li_2O , and 7% P_2O_5 . There are two possible advantages of using Li_2O instead of Na_2O : 1) Li has a much higher boiling point than Na (i.e., 1360°C compared to 892°C) and is less likely to volatilize at the glass-metal interface during the coating operation and 2) Li_2O has a much higher negative free energy of oxide formation than Na_2O and so is less likely to give up its oxygen in a reaction with carbon or another substrate element. In spite of these factors, however, the results were the same as in the phosphorous-free Bioglass test; and there were no observed differences in porosity level for this glass, the phosphorous-free glass, or the standard 52S4.6 Bioglass composition. Various other modifications of either the metal or glass compositions -- such as a reduction of the carbon content of the substrate -- are feasible and might serve to define the primary source of reaction responsible for producing the glass-metal interface during the coating operation.

CHAPTER VIII
BIOLOGICAL, ENVIRONMENTAL, AND FATIGUE TESTING

Fatigue of Glass

Mechanical failure of glass is usually due to brittle fracture. Contrary to the behavior of metals, little or no plastic deformation occurs in glass prior to fracture.⁸³ The strength of glass is much lower than would be expected theoretically because of flaws on the surface. These flaws can act as stress raisers and under an applied load can initiate rapidly propagating cracks which lead to brittle failure of the glass.⁸⁴

The strength of glass decreases when it is held under stress in water or in air containing moisture. In air this decrease in strength depends largely on the amount of moisture present, and this apparently involves a reaction of the glass and the water vapor. A theory of delayed failure of glass in the presence of water has been developed by Hillig and Charles.⁸⁵ In this theory stress-induced corrosion of crack tips in glass due to moisture leads to failure of the glass at low stress levels. Crack propagation and failure occur when the stress at the tip of the crack equals the fracture stress of the glass.

Corrosion of the glass under stress is more important in aiding crack propagation than the amount of corrosion which occurred prior

to introduction of the stress. Under both stress and corrosion influences, flaws can quickly grow to a size where they satisfy the Griffith criterion for crack propagation.⁸⁶ Charles⁸⁷ observed that a high tensile stress at the crack tip leads to an expansion of the glass network in the local area, thus increasing the stress concentration at that point, rather than at the sides of the crack. Any weakening of the glass structure or concentration of stresses caused by localized corrosion leads to a reduction in the fatigue strength of the glass.

Fatigue Behavior of Bioglass

The fatigue behavior of Bioglass is similar to that of other silicate glasses. These glasses can withstand high stresses applied for a short time, but much lower stresses will cause fracture if applied for a sufficiently long period of time. This loss of strength occurs with the application of either a constant or an intermittent load. As an example, the breaking stress of a soda-lime silicate glass similar in composition to Bioglass was observed by Glathart and Preston⁸⁸ to decrease from 20,000 psi at 10^{-2} sec. loading to 7000 psi at 10^5 sec. loading.

The fatigue strength of Bioglass may be greatly influenced by its corrosion and leaching behavior in solution. Bioglass is readily attacked in solution and leaching of Ca, P, and Na ions from the glass must occur in order to establish the proper conditions for the formation of a chemical bond with bone. If this attack occurs at the glass-metal junction of a coated implant or test specimen, then

adherence of the coating will be reduced. Low fatigue strength may be responsible for the failure of the coatings of several Bioglass-metal implants during in vivo testing.

The fatigue behavior of Bioglass-coated metal specimens has been investigated previously by Chhatre et al.⁸⁹ In that study, stainless steel discs which had been flame spray coated with 45S5F Bioglass were tested on an MTS fatigue testing machine. The data showed that the coated specimens could withstand more than 3,000 cycles of loading at 40,000 psi. The fatigue life of similar specimens tested in water was much lower, with failure occurring after an average of only 100 cycles. The fatigue test used was essentially a 3-point bend test in which the flat, coated specimens were supported at three points as a hardened steel pin provided the load. This type of a test is not a true measure of glass-metal interfacial strength, but it did indicate that the overall strength of the glass coating would be lower than tested in solution.

An MTS fatigue testing machine was also used to test the fatigue life (wet) of the Bioglass-coated Vitallium rod specimens used in this study. The test fixture used to hold the coated rod specimens was identical to the two steel cylinders used in the push thru shear test as described in Chapter IV. A hydraulic drive piston was used to compress the cylinders in the test fixture at a prescribed load. The load was applied to a sine wave cycle with a frequency of 10 hertz. Fatigue test results obtained using this set-up are given in Table 16. From this limited number of test specimens, it can be observed that the average fatigue strength of Bioglass-coated-Vitallium is considerably lower than its normal shear strength.

Table 16
Fatigue Strength of the Bioglass Vitallium Bond

Specimen	Kg/cm ² * Force	Cycles to Failure
No Oxide Layer	15.0	200
Oxide Layer too Thick	8.0	150,000
Standard Oxide Layer	12.0	1.4 Million
Standard Oxide Layer	15.0	250,000
Standard Oxide Layer	10.2	2 Million (did not fail)
Standard Oxide Layer	15.0	2 Million (did not fail)
Standard Oxide Layer	38.1	50

*Testing performed at Howmedica, Inc., Groton, CT.

Bioglass-Vitallium Orthodontic Implants

A necessary part of the program to optimize the bonding of Bioglass to Vitallium was to determine how well the coatings adhered during in vitro and in vivo testing. Much of the in vivo testing of Bioglass coated-Vitallium was carried out in conjunction with researchers at the University of Florida and at other universities.

One study at the University of Florida was conducted to determine the feasibility of using Bioglass-coated Vitallium wire as an orthodontic anchor. In orthodontic treatment, a slight tension is used to move teeth into proper alignment over a period of time. This tension can be provided by a thin wire which is anchored either to existing teeth, a brace, or an implant. This study examined the possibility that one end of a wire hook coated with Bioglass and embedded in bone could be used to successfully anchor orthodontic wires or springs, with the Bioglass-bone bond providing the necessary retention.

In vivo evaluation of the bonding of loaded Bioglass-Vitallium wires was accomplished by implantation in rabbits. A preliminary in vivo test was conducted to determine whether putting Bioglass-coated Vitallium wires under stress in physiological solution for a period of six weeks would decrease the adherence of the glass coating. For purposes of this test, a block of soft wood which had been soaked in water for four weeks was used as simulated bone, and holes exactly 12 mm apart were drilled into the surface of the wood. Vitallium-wire implants 7 mm long, 0.85 mm in diameter, and containing a hook on one end were coated in 52S4.6 Bioglass using an

optimized immersion schedule. The coated ends of the test wires were pressed into the prepared holes in the wood, and springs were placed between four pairs of properly spaced wires so that each wire was under a 180 gram load. Other Bioglass-coated wires were placed in the wood but were not loaded in order that the effect of the state of stress on coating adherence could be determined. The block of wood containing both the stressed and unstressed implants was immersed in a tris buffer solution* for six weeks. Other coated wires were left out of the in vitro solution so that any corrosion or static fatigue effects could be monitored.

In order to test the glass-metal bond strength of the coated wires, the hook was removed from each wire and the uncoated end of the wires inserted through a 1.0 mm diameter hole in a 1/16 inch steel sheet. An Instron was used to measure the force required to strip the coating by pulling the wire through the hole in the steel sheet. Table 17 gives the bond strength values obtained from this test. There was no significant difference between the shear strength of the stressed and unstressed specimens which remained in the tris buffer solution for six weeks. However, the specimens which were not placed in the in vitro solution exhibited a higher average bond strength. This indicates that a lower Bioglass coating adherence strength can be expected during use of the coated specimens in a physiological environment.

Similar Bioglass-coated Vitallium wires were implanted in rabbit femurs for a period of three weeks. These wires were placed under

*0.2M tris solution with 0.1M HCl added to obtain pH = 7.4.

Table 17
Bioglass-Vitallium Wire Bond Strengths

Test	N	Mean Kg/cm ²	Std. Dev. Kg/cm ²
Tris Buffer Solution 6 Weeks - Unloaded	7	97.3	8.2
Tris Buffer Solution 6 Weeks - Loaded	6	99.2	5.2
No Solution Unloaded	6	128.8	14.9

spring loads of 60, 120 and 180 grams depending on how far the spring was required to stretch between the implants. At the conclusion of the implantation period, all the coated wires appeared to be firmly fixed to bone. The section of the bone containing each implant was removed, mounted in polyester resin, and ground using 180 grit SiC paper until the top of the hook was reached. A diamond saw was used to cut a specimen 6.0 mm from the top of the wire, so the exact location of the section from the axis of rotation of the implant under load could be determined. Determination of the size of the bone-Bioglass bonding layer on each side of the Vitallium wire was accomplished by EMP analysis in order to determine if the thickness of this bonding layer is affected by its being on the tension or compression side of the implant. The glass coatings on all the rabbit implants examined were well bonded to the metal, and no corrosion was observed at the glass-metal junction or in any location of the implant surface.

Implant-Tissue Interfacial Study

A study is currently being conducted at Tulane University to determine the effects of various types of implant surfaces on the surrounding tissues. The different materials being studied include smooth carbon, materials with porous surfaces, and Bioglass-like materials which form a chemical bond to bone. The character and biomechanical behavior of the implant-tissue interface for each material is being evaluated after a six month implantation period in dog femurs.

For purposes of this study, eight hollow Vitallium castings (8 mm in diameter by 50 mm long) were coated with 52S4.6 Bioglass using

an optimized immersion coating procedure. The glass coating on each specimen was ground so that the implant would fit snugly into a 10.0 mm diameter hole prepared in the canine femur. After implantation of the coated Bioglass-Vitallium "plugs," the dogs were restrained from using their legs for only one day before being given full mobility.

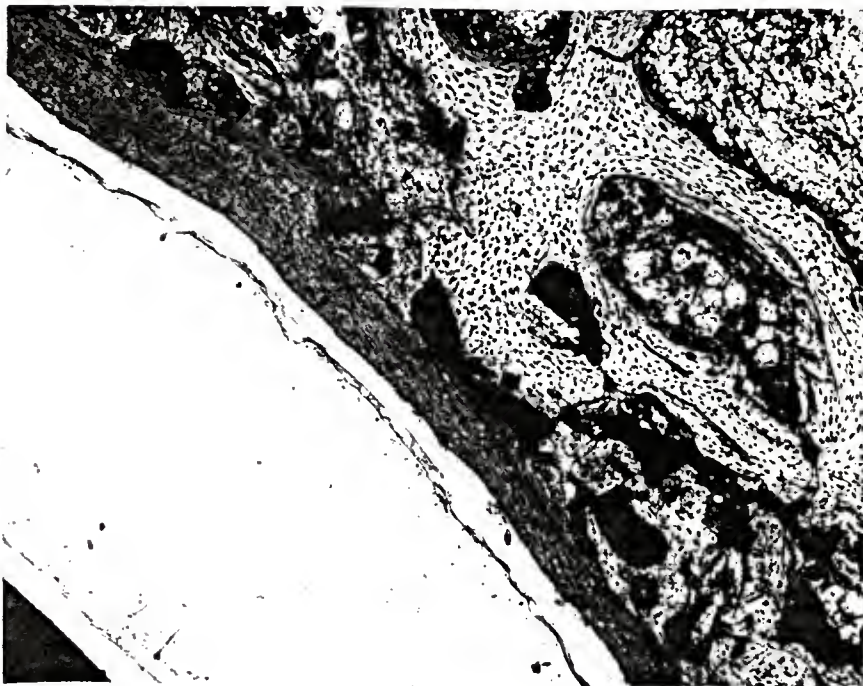
The first Bioglass-coated implant examined was from an animal which broke both legs and had to be sacrificed before the scheduled six month's implantation term was completed. The section of the femur containing the implant was removed and the tissue dehydrated using graduated alcohol solutions with the final step being a 100% alcohol rinse. After the drying procedure, the bone-implant section was embedded in poly methylmethacrylate and sliced into 300 μm sections using a wafering saw with a low concentration diamond blade. Each section was ground to 150 μm using a precision swivel-head grinder. The thin sections were then cemented to a glass slide and ground to 50 μm .* A polychromatic stain (Paragon 1301) was used to prepare the tissue for microscopic observation. The 50 μm section is thicker than that normally examined by the transmitting optical microscope, but the stain was only allowed to penetrate 10 μm in depth so good tissue detail was retained.

Examination of the prepared slides using an optical microscope showed that a fibrous capsule had formed around the implant surface (Fig. 14). As the implant was subjected to load within one day after

*Specimens ground and mounted at Tulane University.



(a)



(b)

Figure 14. Scanning electron micrographs (40X) of the Vitallium (black) - Bioglass (light) - tissue cross section of a canine femur implant. (a) and (b) are sections near the opposite ends of the implant.

surgery, there is a high probability that excessive movement interfered with the bone-Bioglass bonding mechanism resulting in the formation of a thick capsule around the implant rather than a chemical bond with the developing bone structure.

The Bioglass coating was found to be strongly bonded to the bulk of the implant, and no corrosion at the glass-metal junction was observed. However, the porosity which is commonly observed at the glass-metal interface of most Bioglass-Vitallium specimens was also seen in this case (Fig. 15). Examination of additional Bioglass-Vitallium implants which went the full six months of this in vivo test showed that there was excellent coating adherence in all cases.

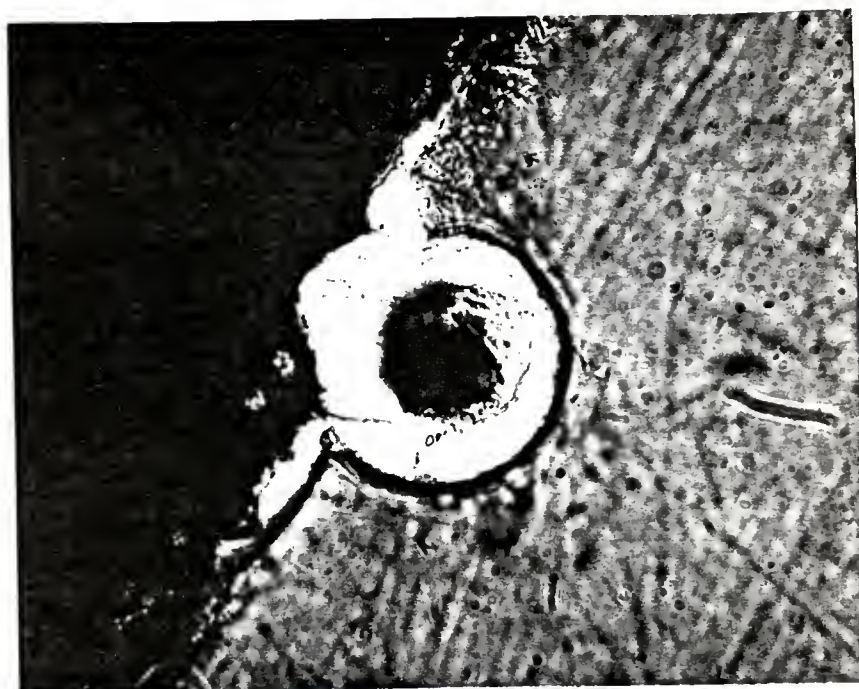
Bioglass-Vitallium Endosseous Implants

A study was conducted to determine if Bioglass-coated-Vitallium mandibular implants were sufficiently compatible with the surrounding tissue so that epithelial attachment to the implant occurred. Small egg-shaped Vitallium implants were immersion-coated in 52S4.6 Bioglass at the University of Florida, and sent to the University of Washington where they were implanted in the mandibles of monkeys.⁹⁰ After surgery the implant sites were left undisturbed for six weeks to allow the healing and new bone formation. After six weeks a short Vitallium post holding a bone wafer was placed in a prefabricated hole in the top of the implant.

The implants and surrounding tissues were removed after ten weeks and decalcified in ethylene diamine tetra acetic acid. After demineralization the tissue was separated from the implant by scraping with



(a)



(b)

Figure 15. SEMs of porosity at the interface of a Bioglass-Vitallium canine implant.

- (a) Metal-glass tissue interface (40X)
- (b) 75 μm pore at the glass-metal-interface (400X)

a sharp razor blade. The tissue was then sectioned and stained with various preparations such as Schiff's reagent.*

Histological and SEM examination of the tissue around the implant showed that in most cases the expected soft tissue seal was not present. Several of the basic criteria for implant-tissue attachment were not satisfied, as there was little evidence of attachment of the periodontal ligament or of collagen fibers oriented perpendicular to the implant surface. The observed lack of attachment may be the result of inflammation which developed in most of the prepared sockets or the damaging (and removal in some cases) of the implants by the monkeys prior to the conclusion of the experiment.

As in the other in vivo studies, all the Bioglass coatings were found to be well bonded to the Vitallium implants, with no cracking or flaking of the glass from the metal surface. Also there was no evidence of corrosion at the glass-metal junction of any of the implants, indicating that the immersion coating process does not cause sensitization of the Vitallium resulting in a reduction of its corrosion resistance.

*Prepared at the University of Washington.

CHAPTER IX ANALYSIS OF THE GLASS-METAL INTERFACE

Objective of Interfacial Analysis

The primary objective of this research was to determine the nature of the bond formed between a glass and metal. After the effect that each variable in the coating process has on bond strength was determined, the focus of the investigation was shifted towards the characterization of the Bioglass-Vitallium interfacial region by the use of various analytical techniques.

One means of gaining an understanding of which microstructural factors are of primary importance in glass-metal bonding is to compare the interfacial characteristics of specimens having a high bond strength with those having low bond strength. One of the structural factors which can be readily monitored by various techniques (e.g., SEM) is the oxide layer which is present between the glass and metal. Important features of this oxide layer are its composition, thickness, continuity and roughness. Another characteristic of the interface which can be determined by AES and EMP analysis is the presence of metallic ions in the glass and ions from the glass in the metal. The diffusion of these ions across the interface during the coating and subsequent heat treating operations establishes compositional profiles which are characteristic of the type and strength of bond formed between the glass and metal.

Electron Microprobe Analysis

The electron microprobe (EMP) was used in this study to determine the total distance of diffusion of ions across the glass-metal interface. An EMP analysis of the interfacial region of a typical immersion coated Bioglass-Vitallium specimen is given in Fig. 16. It can be observed that only limited diffusion of ions from the metal into glass or from glass into metal occurred during the short time interval of immersion coating (3 sec. at 1350°C).

Figure 2 shows the diffusion pattern of a similar specimen which was given an additional heat treatment of 3 hrs. at 800°C. The diffusion profiles are quite different from the previous case, with Co diffusing well into the glass (approximately 25 μm) and Cr remaining more concentrated near the interface. However, even with the extended heat treatment, only limited diffusion of ions from the glass into the metal occurs.

Although EMP is useful for determining the total distance of diffusion of each ion, the penetrating nature of the X-rays used in compositional analysis makes this technique ineffective for analyzing changes in composition in the narrow interfacial region (which is typically less than 2 μm wide for immersion coated specimens). The EMP also has the disadvantage of having a beam size of greater than 1 μm , so analysis points are typically 2 μm or more apart.

Scanning Electron and Light Microscopy

Scanning electron microscopy (SEM) and light microscopy (LM) were used to characterize the topography of the fracture surfaces

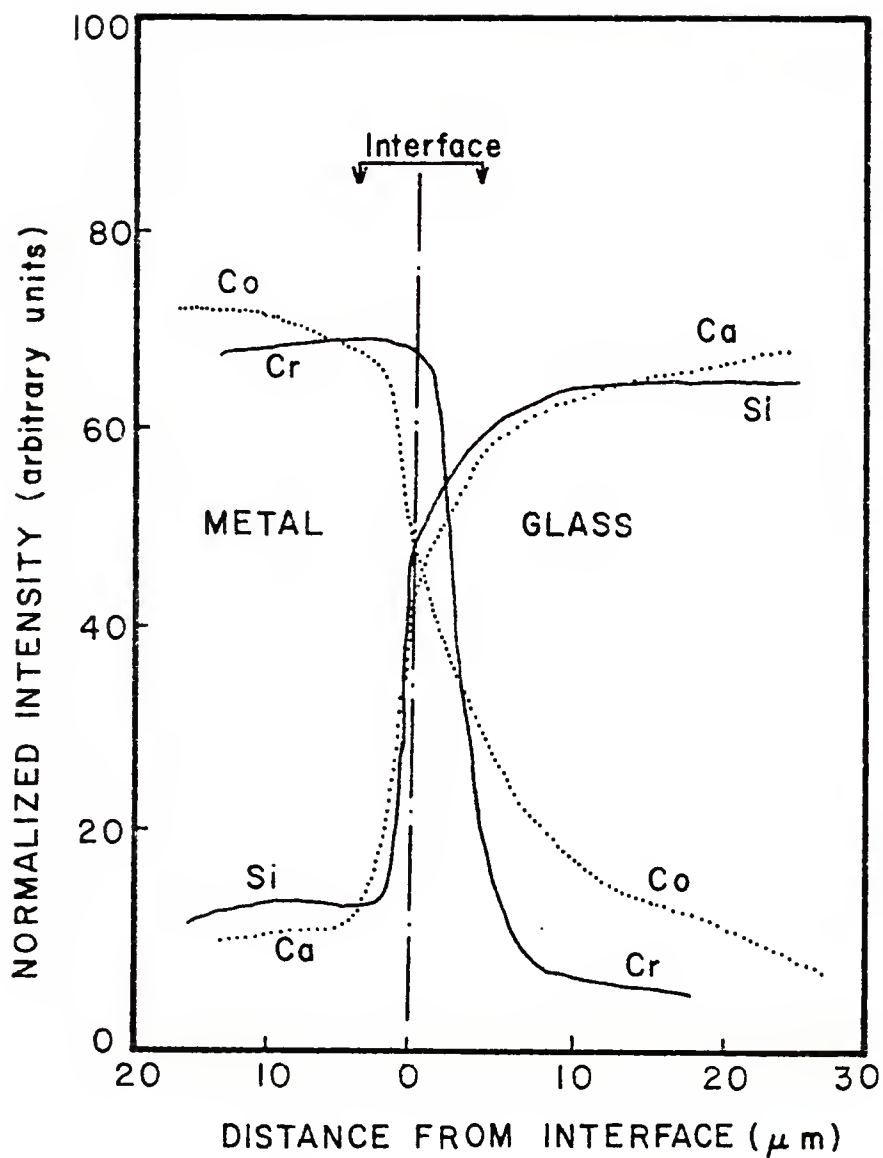


Figure 16. Electron microprobe analysis of a Bioglass-Vitallium specimen showing diffusion of ions across the interface following a heat treatment of 800°C for 3 hrs.

so that a correlation of bond strength and surface characteristics could be made. Figures 7b and 17 are SEM micrographs showing an oxidized surface and a fracture surface of identical Vitallium specimens. The most noteworthy difference in the fracture surface is the presence of scattered glass pieces. This indicates that failure did not occur only at one interface (e.g., the metal oxide layer) but was mixed-mode in nature. A high magnification view of these glass pieces and the surrounding metal fracture surface is given in Fig. 18. For purposes of comparison, the metal fracture surfaces of a specimen which exhibited a poor bond and one which had a good glass-metal bond are shown in Fig. 19a and 19b, respectively. As the number and size of the remaining glass pieces appeared to vary from specimen to specimen, an attempt was made to correlate this observation with the measured bond strength. Quantitative microscopy techniques as discussed by Hilliard⁹¹ were used to determine the area fraction of glass on a number of specimens with varying bond strengths. However, it was observed that there was no significant difference between the average area fraction of glass on the metal fracture surfaces of poor-bond specimens ($A_A = .16$) as compared to that of good-bond specimens ($A_A = .13$).

Porosity which is present at the Bioglass-Vitallium interface is typically observed in SEM and LM micrographs. The imprint of various bubbles in the glass fracture surface of a typical specimen can be seen in Fig. 20. These pores or voids range from approximately 1 μm to 100 μm in diameter. An LM view of a bonded glass-metal interface shows a 75 μm bubble in the glass layer at the

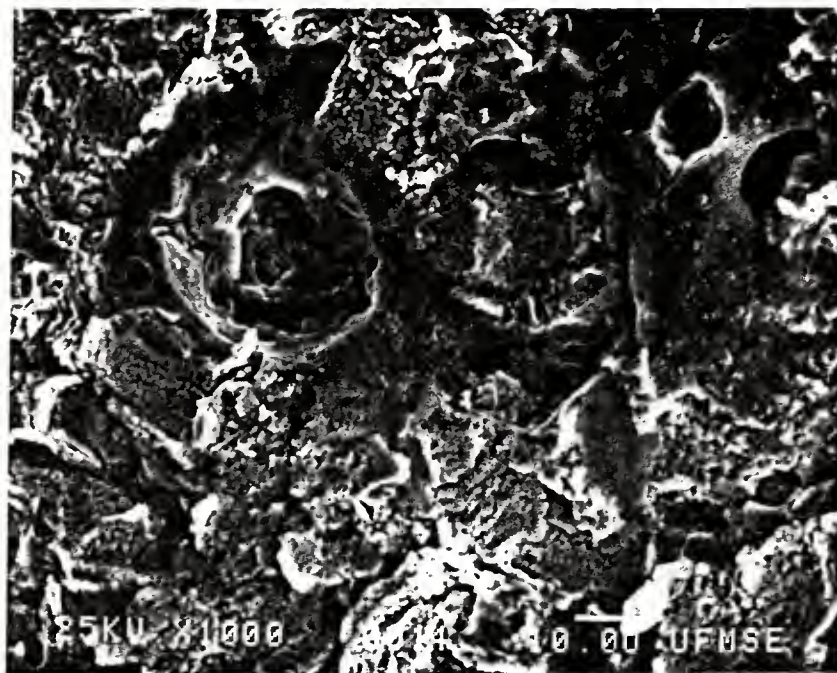
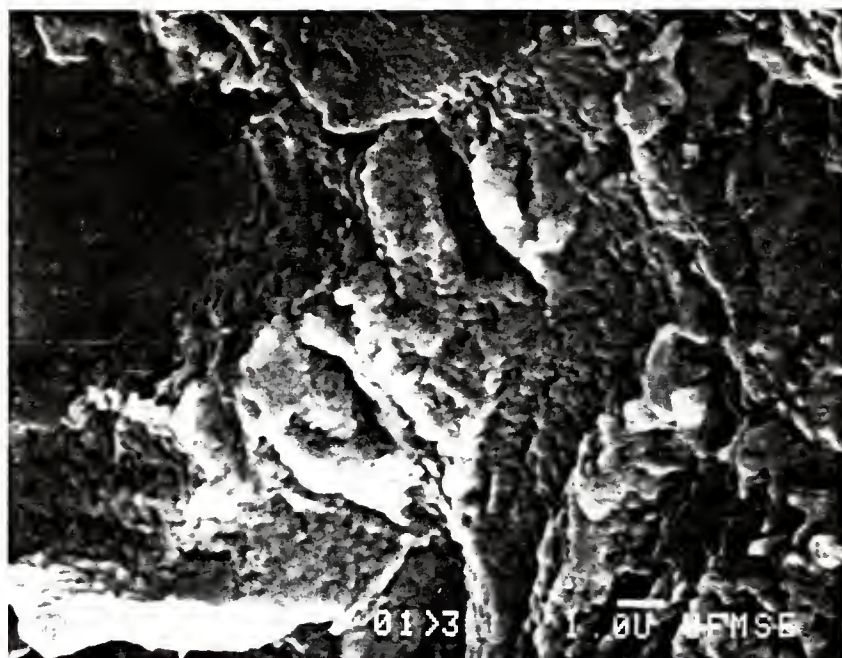
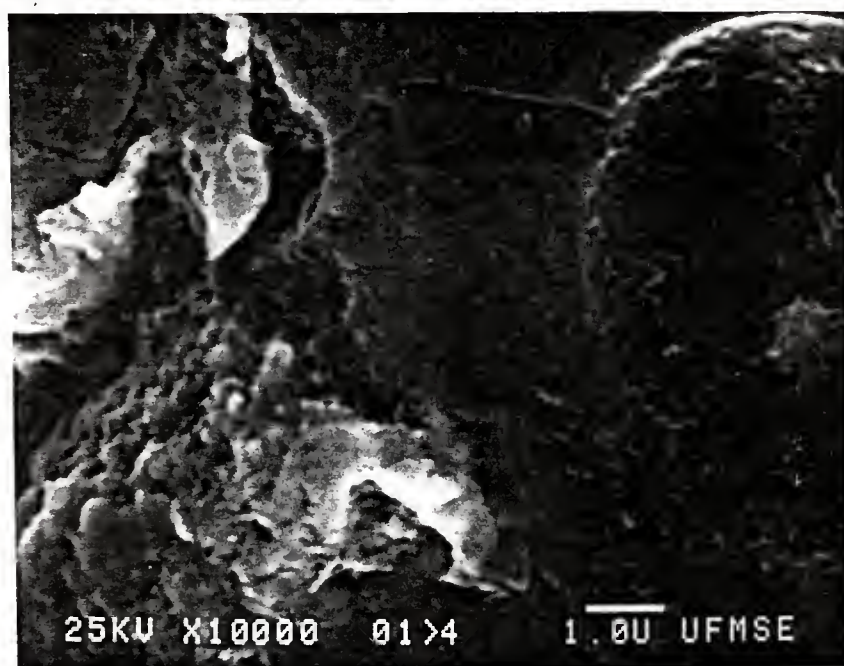


Figure 17. Scanning electron micrograph showing Vitallium Fracture Surface with scattered glass pieces remaining (1000 X).



(a)



(b)

Figure 18. Scanning electron micrographs showing the junction of glass pieces to the oxidized metal surface.

(a) Glass piece in a normal surface cavity (6000X).

(b) Glass piece with 5 μm pore (10,000X).

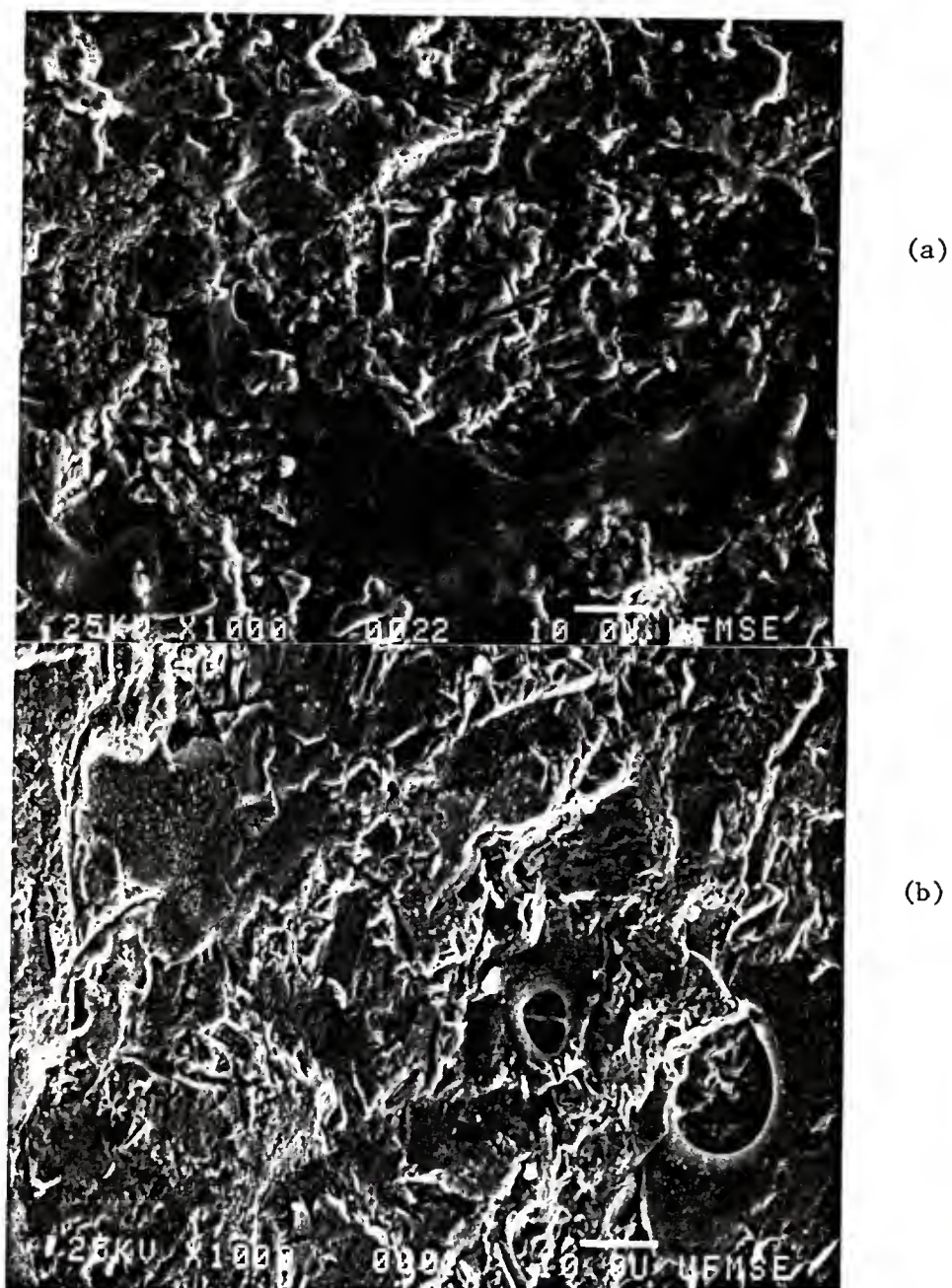


Figure 19. Scanning electron micrographs (1000X) of metal fracture surfaces showing glass pieces remaining after shear testing.

- (a) Specimen with poor bond strength.
- (b) Specimen with good bond strength.

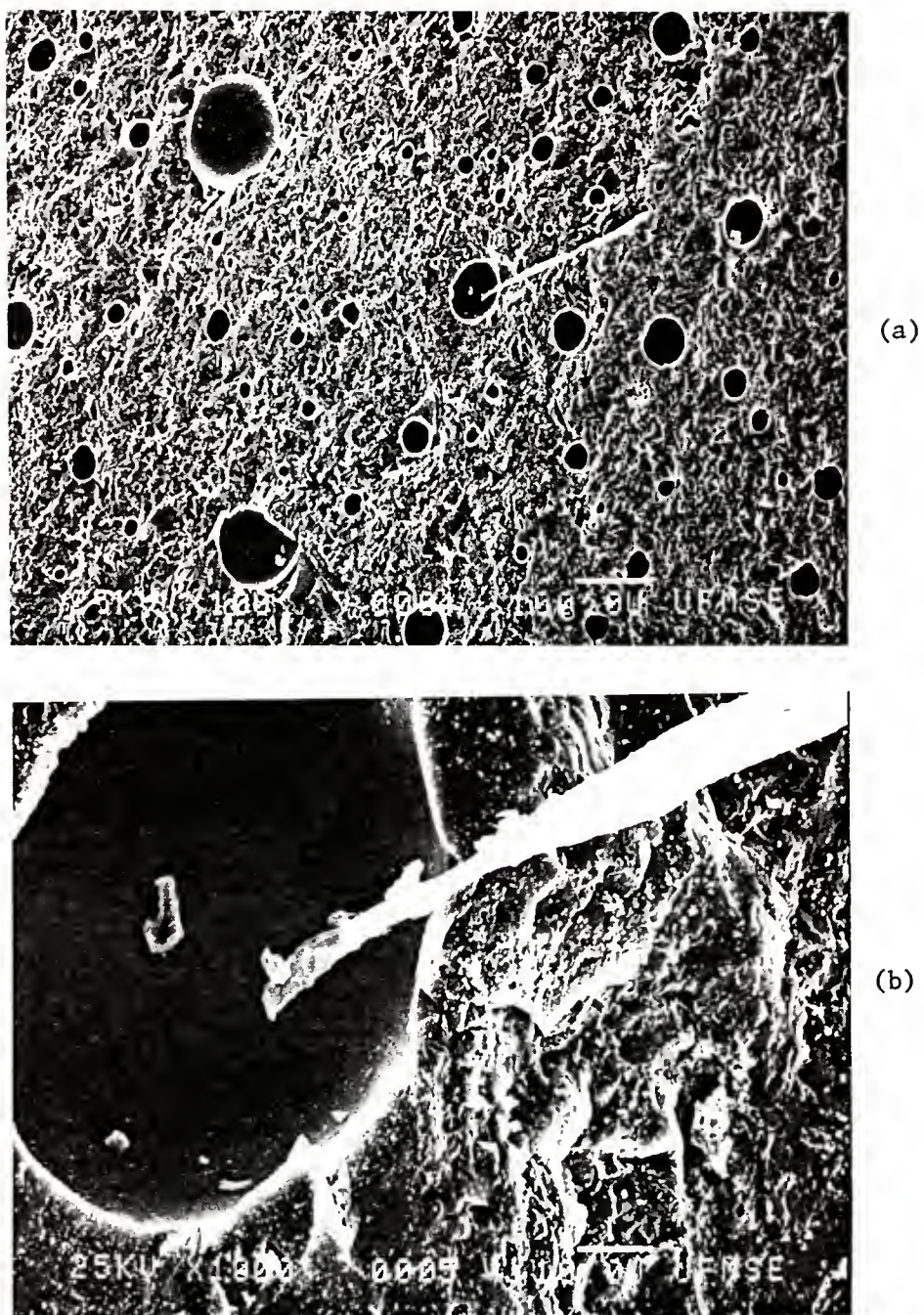


Figure 20. Scanning electron micrographs of pores in the glass section of a fracture surface:

- (a) Distribution of pores (1-100 μm) in the fracture surface (100X).
- (b) Pore-glass interface with glass fragment remaining for shear testing.

interface. A premature fracture line can often be observed to pass through an interfacial pore such as this.

On the double coated specimens, much of the thin, inner layer of Bioglass coated by the frit enameling method generally remained after shear testing (Fig. 13). The fracture path on these specimens was very irregular, and could have started at either the metal-glass interface or between the layers. If the inner coating was excessively thick and porous because of poor particle condensation or insufficient firing, failure was primarily confined to this layer. Bubbles were observed at the interface between the two glass layers in several cases and their presence was attributed to diffusion of gas through the somewhat porous (i.e., underfired) inner glass layer.

Auger Electron Spectroscopy

Auger electron spectroscopy (AES) has been shown to be a valuable technique for the surface analysis of materials, with its primary advantage being the small escape depth of the Auger electron (less than 50 Å). In conjunction with ion milling, compositional changes over distances of only 10's of Å can be determined.

In this study, the glass coatings were stripped off the metal specimens during shear testing, then metal and glass fracture surfaces were analyzed separately using AES. Care was taken to analyze points on the glass and metal surfaces which were from the same location on the original (unfractured) interface. The results from the two analyses were plotted on the same graph to give the compositional

profiles on both sides of the interface. The peak heights of the elements of interest were measured and these values were normalized in order to give a more accurate indication of relative composition (see Chapter III). Often the previously normalized values of Cr and Co were plotted as a ratio (i.e., Cr/Co) to eliminate the effects of variations in the beam current and the partial pressure of argon. As AES analysis revealed only trace amounts of Mo in the glass and negligible diffusion of Si, Na, Ca, and P into the metal, none of these elements were included in the compositional profile.

In order to determine the specific compositional profiles which are associated with the condition of good glass-metal bonding, specimens which had been shear tested were divided into three groups based on bond strength and oxide layer thickness:

Group I (B) - low bond strength ($40\text{--}50 \text{ Kg/cm}^2$ average), thick oxide layer (greater than $0.4 \mu\text{m}$).

Group II (A) - high bond strength (greater than 80 Kg/cm^2), moderate oxide layer ($0.2\text{--}0.3 \mu\text{m}$).

Group III (C) - low bond strength (less than 40 Kg/cm^2), very thin oxide layer ($0.1 \mu\text{m}$ or less).

Tables 18 and 19 give typical data of the AES analyses of metal fracture surfaces of Group I (B) and Group II (A) specimens. Figure 21 shows that for both good and poor bond specimens there is a much higher level of Cr present in the glass as compared to Co, with a Cr peak occurring about $0.2 \mu\text{m}$ from the interface. As a comparison, the Cr/Co ratios in the glass for the same specimens are plotted in

Table 18

AES Analysis of Metal B (Poor Bond) Fracture Surface

Peak Height Measurements (mm) to 101 Min. Ar Milling Time Cr/Co: After Normalization							
Time (Min)	C	O	Cr	Co	Cr/O	Co/O	Cr/Co
0.5	22.8	46.0	1.5	1.45	.032	.031	2.30
1.5	25.0	43.0	1.2	1.95	.027	.045	1.34
3	22.5	39.5	2.1	2.7	.053	.068	1.74
6	21.5	40.0	3.0	8.5	.075	.212	.789
12	15.5	31.5	4.8	11.6	.152	.368	.921
20	11.5	30.6	5.2	13.5	.169	.441	.854
26	10.5	29.5	5.5	13.9	.186	.471	.880
34	9.8	28.0	5.4	13.7	.192	.489	.876
41	10.0	29.2	6.7	17.2	.229	.589	.867
50	9.6	27.5	6.7	15.7	.243	.570	.950
62	9.2	27.2	6.3	16.0	.231	.588	.876
74	8.0	24.9	6.2	15.0	.248	.602	.919
84	7.2	23.8	6.0	14.8	.252	.621	.95
101	8.0	25.0	8.3	18.0	.332	.720	1.03

Table 19

AES Analysis of Metal A (Good Bond) Fracture Surface

Peak Height Measurements (mm) to 50 Min. Ar Milling Time Cr/Co: After Normalization								
Time (Min.)	C	Ca	O	Cr	Co	Cr/O	Co/O	Cr/Co
0.5	32.0	3.8	60.8	.64	3.6		.059	
1.5	35.0	4.0	55.5	3.7	5.5	.011	.099	.248
3	26.2	3.5	45.0	4.5	9.2	.082	.204	
6	19.5	2.3	36.2	7.5	13.0	.124	.359	.770
12	14.0	1.9	30.0	7.0	19.8	.25	.660	
20	10.5	1.5	24.9	7.5	18.2	.281	.730	.858
26	9.2	1.5	24.1	7.6	17.5	.311	.726	
34	8.0	1.2	22.9	10.2	17.9	.331	.781	
41	12.0	1.3	26.0	9.5	27.0	.392	1.03	.874
50	9.8		25.5		23.0	.372	.901	.921

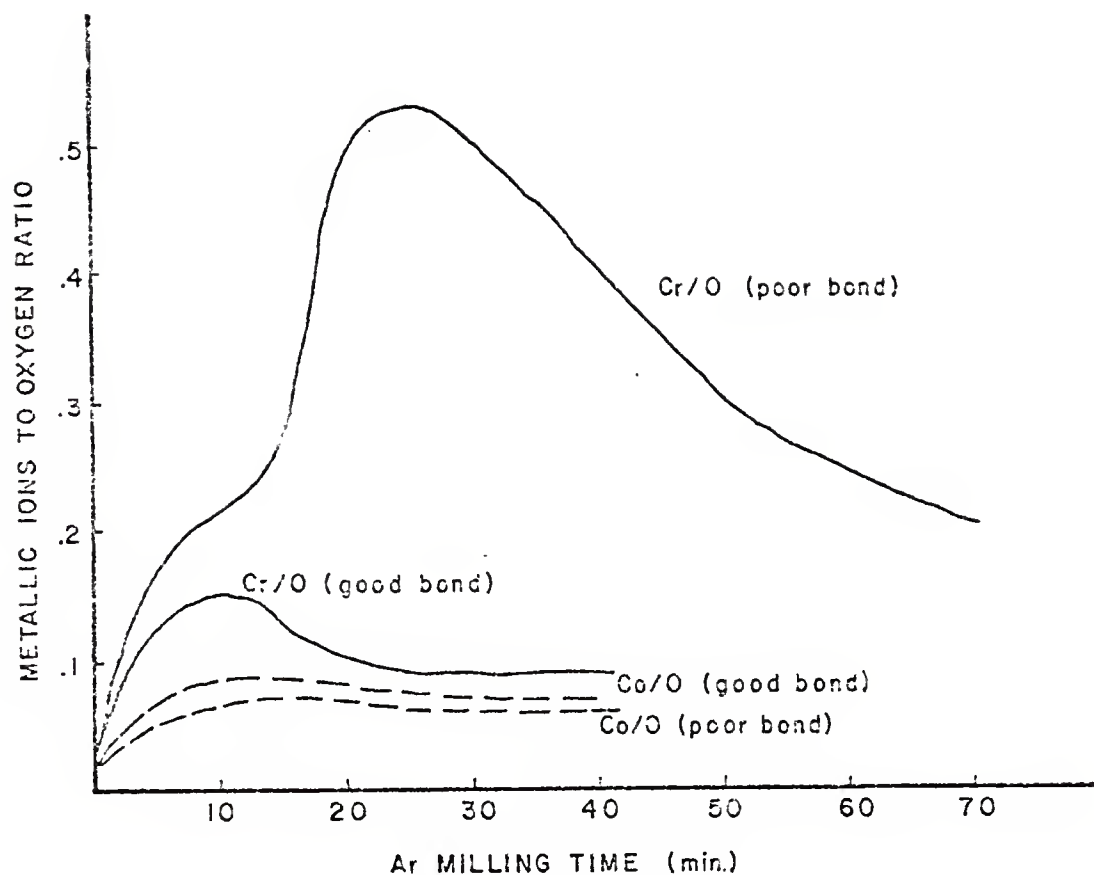


Figure 21. AES analysis showing the ratio of metallic ions to oxygen in the glass.

Fig. 22. A Cr/Co ratio of 1 reflects the base alloy composition after normalization, so a Cr/Co ratio of greater than 1 indicates a higher than normal level of Cr. In both the figures it is apparent that the level of Cr in the glass layer of a specimen with a low bond strength (Group I) is much higher than that in a specimen with a good bond strength (Group II). In Fig. 23, the plot of the Cr/Co ratios in the metal interfacial region (opposite the analysis point taken on the glass surface) shows high Cr for the Group I (B -- poor bond) specimen and low Cr for the Group II (A -- good bond) specimen.

The AES analyses of the complete interfacial regions of typical specimens of Groups I, II, and III are given in Fig. 24. These results show clearly that Group I specimens failed in an area of high Cr content, while Group II and Group III specimens fractured in areas of lower Cr.

Analyses of the interfacial areas of crystallized (ceramed) Bioglass-Vitallium specimen and a dental porcelain-Vitallium specimen are shown in Fig. 25. The Cr/Co profiles of these two specimens are similar, with both having high Cr in the glass phase and a wide Cr-depleted zone in the metal. The extended time at temperature which allows diffusion to continue (either during the coating or crystallization operations) is responsible for the differences between these Cr/Co profiles and those for typical immersion coated Vitallium specimens.

Discussion of AES Results

The compositional profile of the oxide layer on Vitallium had previously been shown by AES to consist of a high Cr layer with a

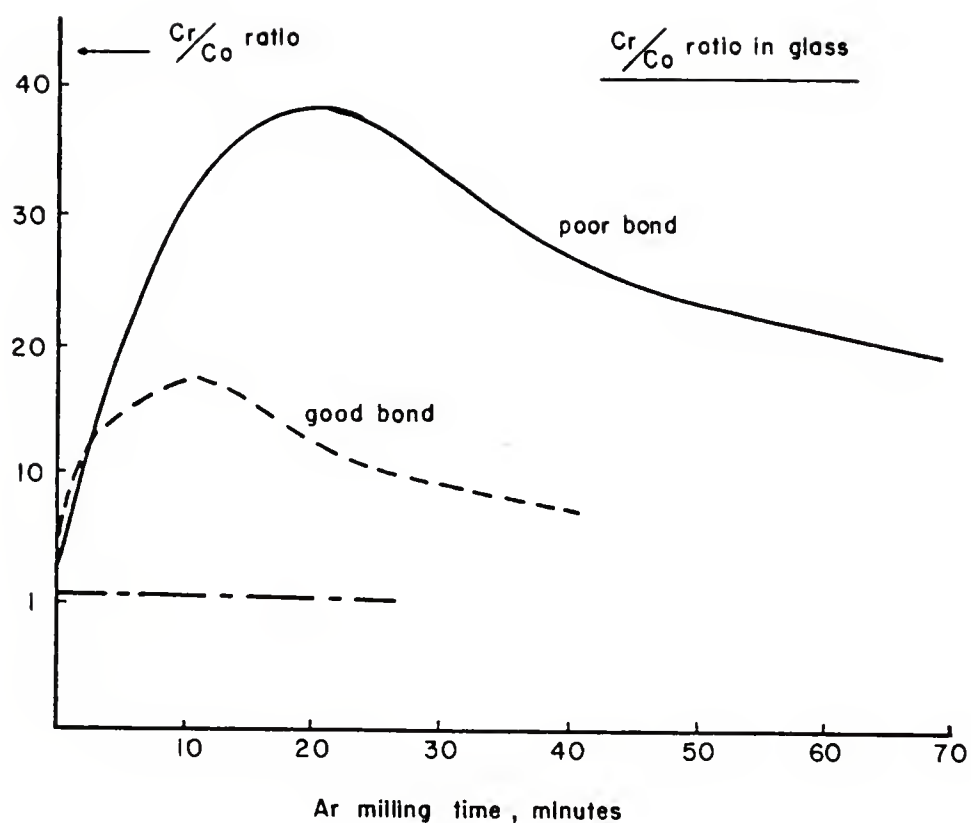


Figure 22. Auger electron spectrographic analysis of a Bioglass fracture surface. A higher Cr/Co ratio is present in the glass layer of a specimen which had exhibited a low bond strength.

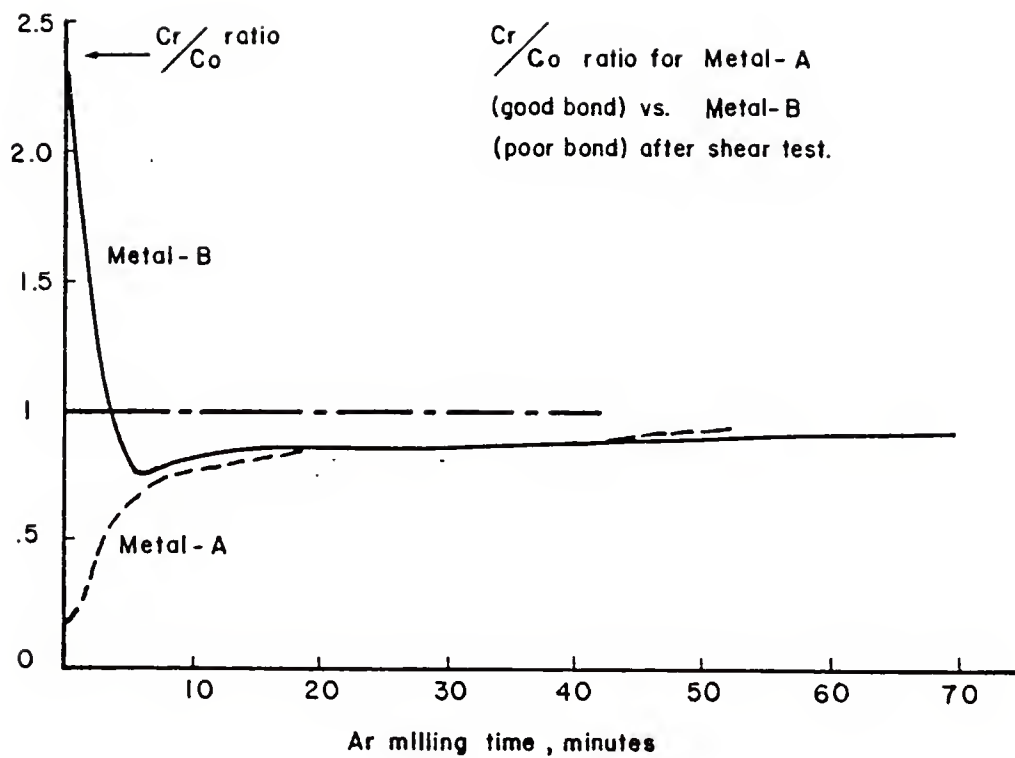


Figure 23. AES analysis of the metal interfacial region of good and poor bond specimens.

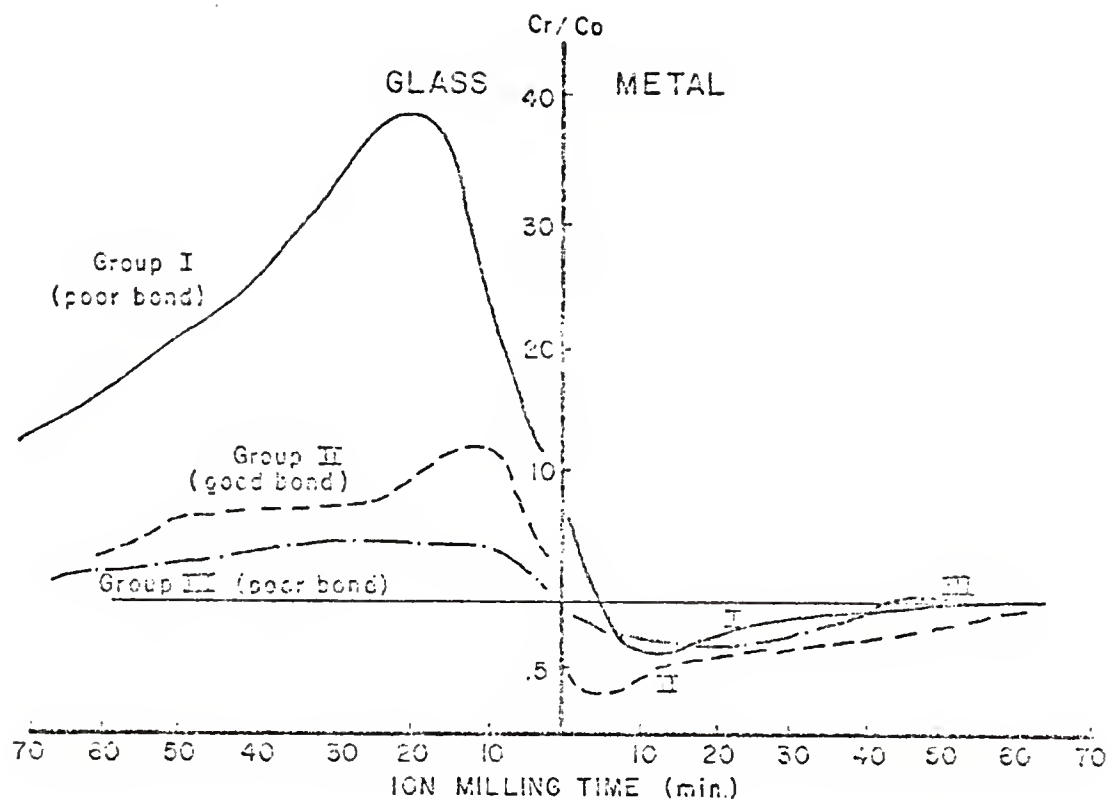


Figure 24. AES analyses of specimens from Groups I, II, and III.

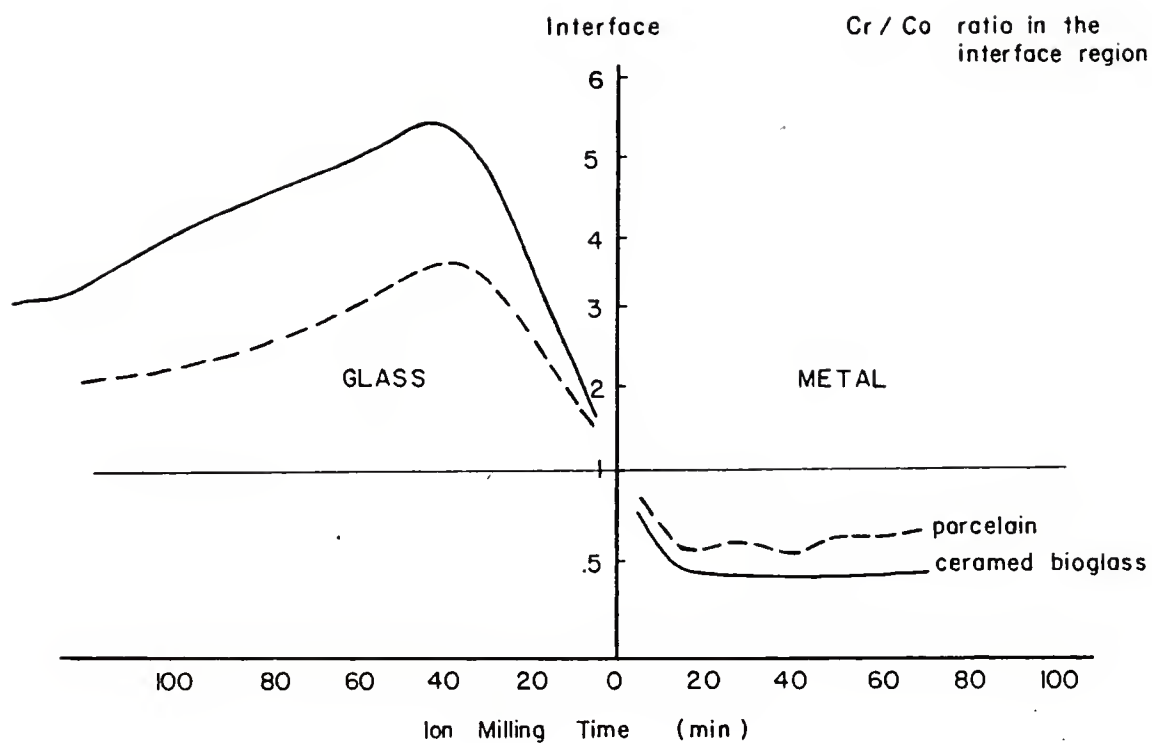


Figure 25. AES analyses of a Bioglass-dental porcelain specimen and a ceramed Bioglass-Vitallium specimen.

Cr-depleted zone between the Cr_2O_3 healing layer and the bulk metal composition. As seen in Fig. 24, this same pattern of Cr and Co diffusion is typically found in the glass at the interface after the immersion coating operation. This demonstrates that the molten glass has absorbed at least part of the oxide layer during the immersion coating operation.

Group I specimens (poor bond strength) generally have oxide layers which are thicker than $0.4\text{ }\mu\text{m}$. The high Cr in both the metal and glass fracture surfaces for this group of specimens is an indication that fracture occurred predominately with the oxide layer, similar to the Class V fracture described by O'Brien.⁷⁶ However, SEM micrographs (such as in Fig. 19) show that the metal fracture surface contains small pieces of the glass phase, so the fracture path is obviously not confined to just the oxide layer. This type of fracture pattern can be best described as mixed-mode, and similar fracture has been observed by Anusavice to occur for the Ni-Cr-bonded-to-dental porcelain system.⁹²

The specimens with the highest bond strength (Group II) generally fractured along the interface between the oxide and the metal. The low Cr/Co ratio at the metal interface is characteristic of the depleted zone between the Cr_2O_3 layer and the bulk alloy composition. For Group II specimens, the oxide layer on the metal has been absorbed by the molten glass to a point where only a small amount of oxide remains. Based on the bond strength results, this is the condition at which maximum glass-metal adherence is attained.

Class III specimens had low bond strength due to minimal oxide layer formation prior to the coating operation. These specimens were either oxidized at a low temperature (e.g., 350°C) or were given no oxidation treatment at all prior to immersion coating. There is a slight Cr peak in the glass with a corresponding Cr-depleted zone in the metal, indicating that some oxidation had occurred. However, SEM examination showed that the oxide formed on the metal was patchy, indicating that islands of oxide (primarily Cr_2O_3) had formed rather than a continuous layer.

From these results, it is clear that there is an oxide layer thickness which is optimum for maximum glass-metal adherence under a given set of conditions. Oxide layers which are too thin are quickly dissolved by the molten glass and do not maintain the conditions necessary for good chemical bonding. Oxide layers which are too thick may also be detrimental to good adherence, as failure may occur within this layer at a low stress level. The maximum glass-metal adherence occurs when the molten glass absorbs the oxide layer until only a thin (but finite) amount of oxide remains on the surface of the metal.

Factors Important to Bond Strength

The analyses of specimens with both high and low bond strengths had shown that the thickness of the oxide layer on the metal substrate is the key factor which determines the strength of the glass-metal bond. By the knowledge of the Cr/Co profile for a particular specimen,

one can predict both the original oxide layer thickness and the approximate bond strength for that specimen (for a given set of immersion coating conditions). However, if similar specimens are given a heat treatment, the increased diffusion of metal ions creates entirely new Cr/Co profiles and alters the conditions required for maximum bond strength. For example, coated specimens which were given a crystallization treatment (3 hrs. at 800°C) were observed to have an average of 40% lower bond strength (see Table 20) as compared to identical specimens which were not given this thermal treatment.

Determination of the reasons behind this loss of bond strength with prolonged heating is important in resolving some of the uncertainties about the nature of the glass-metal interface, and is necessary to define what factors are most important for good bond strength. Several of the possible explanations as to the primary cause of the observed loss of glass-metal adherence are:

1. Crystallization changes the expansion coefficient of the glass, thus increasing the stress at the glass-metal interface so that microcracks are produced during cooling.
2. Excessive metal oxide diffusion away from the interface leaves the glass layer at the interface in an unsaturated state so that chemical bonding is partially lost.
3. Cr and Co diffusion into the glass drastically lowers the thermal expansion coefficient of a portion of the glass coating; thus causing thermal mismatch and the development of a highly stressed layer at the interface (as proposed by Sced and McLean⁵⁷).
4. Additional reactions occur during prolonged heating, generating gas which is trapped at the interface as bubbles.
5. Crystallization raises the softening point of the glass, causing an increase in stress at the interface due to thermal expansion differences over a wider temperature range.

Table 20

Effect of Glass Heat Treatment on Bond Strength

Specimen	Heat Treatment	N	Mean Kg/cm ²	Std. Dev. Kg/cm ²
52S4.6 Bioglass	None	6	69.2	2.9
52S4.6 Bioglass	Crystallized at 800°C for 3 Hrs.	6	42.3	4.6
52S4.6 Bioglass	Heat Treated at 800°C for 3 Hrs. Not Crystallized	4	45.8	6.2

6. Increased diffusion of metal ions into the glass causes a flow of vacancies to the glass-metal interface, thus forming voids which decrease adherence.

Dilatometer measurements were made on both crystallized and uncrystallized Bioglass rods to determine the effect of the crystallization treatment on the thermal expansion coefficient of the glass (Table 15). A partly crystalline specimen (i.e., 70% crystalline) had only a 1.5% lower thermal expansion coefficient than the measurement taken before it was subjected to the crystallization treatment. Using the relation:

$$S = 1.13 \Delta\alpha\Delta TE$$

where: α is the coefficient of thermal expansion

F is the average of the elastic moduli,

the calculated hoop stress (S) is only 13.6 Kg/cm^2 , not sufficient in magnitude to cause the reduction in shear strength observed.

Also, specimens coated with 45S5F glass --whose α differs from that of Vitallium by a wider margin than crystallized 52S4.6--had shear strengths similar to those of uncrystallized 52S4.6 specimens.

Specimens which were given the same heat treatment but were not crystallized showed a similar decrease in glass-metal adherence. These specimens (which were cooled from the coating operation to 800°C and held at this temperature for 3 hrs.) showed only minor light scattering indicative of a very small amount of crystal formation. Thus the degree of crystallinity of the glass coating was eliminated as the cause of the lower bond strength of the heat treated specimens.

Porosity at the glass-metal interface is often a cause of low bond strength, as even 10% void space in the interfacial area can reduce the adherence in half. However, there was no observable increase in the porosity level at the interface due to the thermal treatment. The crystallization temperature of 800°C is too low to cause further glass-metal reactions in which more gas (e.g., CO₂) is liberated.

Electron microprobe results showed that prolonged heating during crystallization treatment (3 hrs. at 800°C) causes much greater diffusion of chromium and cobalt into the glass coating than the 3 sec. immersion period (at 1350°C). Figure 16 shows Cr diffusion to be 10 μm and Co 25 μm into the glass from the interface. From EMP and AES data, it is difficult to prove or disprove Sced and McLean's⁵⁷ theory on the effect of the change in α due to Cr and Co diffusion. There is a higher level of Cr and Co in the glass as a result of the increased diffusion, however, these ions are not concentrated at the interface. Therefore, with the metal ions spread over a much wider zone, a gradient of thermal expansion values is established which would tend to reduce the effects of thermal mismatch.

The theory proposed by Pask⁴¹ and others that the loss of saturation of metal oxide at the interface leads to lower bond strength fits well the observations made in this study. There is no atmospheric oxygen available when the glass covers the substrate metal, so any oxygen supplied at the interface must come from the reduction of a component in the glass. Based on the standard free energies

of oxide formation (Table 3), it is not possible for Co to reduce any oxide in the glass. On the other hand, reduction of P_2O_5 and Na_2O by Cr is possible, but may not occur to the extent necessary to keep the interface saturated (due to the relatively low thermodynamic driving force at $800^\circ C$). Also, Cr may diffuse to locations well away from the interface before being oxidized, so is not available at the interface where saturation is critical in maintaining the continuous electronic structure.

A number of investigations on the oxidation behavior of Co-Cr alloys^{66,71} have found that the accumulation of vacancies at the metal-metal oxide interface during the oxidation process is responsible for lower oxide scale adherence. These vacancies are produced by the movement of metal cations to the surface of the metal. A healing layer of Cr_2O_3 is necessary to limit further oxidation and thus prevent the formation of voids at the interface. However, the thin oxide layer necessary for optimum bonding of immersion coated specimens (about 0.2 to 0.3 μm) is somewhat discontinuous and non-protective when partially dissolved by the molten glass. Mackert⁹³ found that the outward diffusion of Cr from a nickel-chromium alloy into porcelain continues during heating if the Cr_2O_3 oxide layer is not protective enough. He found that the strengthening of the oxide layer by the addition of Al (in the form of a "bonding agent") greatly restricts the outward flow of metal ions during heating, and results in decreased void formation at the interface. In the case of Bioglass-Vitallium, the thin oxide layer necessary for optimum

bonding of immersion coated specimens (approximately 0.2 to 0.3 μm) is somewhat discontinuous and too thin to be protective after being partially dissolved by the molten glass.

In summary, the continued heat treatment of Bioglass-coated-Vitallium at a sufficiently high temperature (800°C or greater) causes a loss of bond strength. The thin, partially dissolved Cr_2O_3 layer on the metal substrate is not protective enough to prevent the diffusion of metal ion into the glass phase. The decrease in metal ion saturation in the glass at the interface and the formation of voids at the glass-metal interface results in low glass-metal bond strength. To prevent loss of bond strength during prolonged heating, a more protective oxide layer should be formed on the metal surface, and this layer should be thick enough so that it is not dissolved during the coating operation.

CHAPTER X SUMMARY AND CONCLUSIONS

Bioglass-to-Vitallium Bonding

This investigation into the nature of the bonding between Bioglass and Vitallium was able to identify several characteristics of a good bond which are common to glass-metal systems in general. The effect of various factors (such as surface roughness) on glass-metal adherence was determined quantitatively by the use of a shear strength testing method. These results showed that the adherence between glass and metals is more dependent on chemical bonding than on mechanical interlocking.

During the oxidation of Vitallium, a high-Cr oxide (Cr_2O_3) is formed on the surface with a Cr-depleted zone between this layer and the bulk metal. The pressure of oxygen during heating affects only the total depth of oxidation, not the characteristic Cr and Co profiles. The compositional profile of Cr is retained at the interface between glass and metal after immersion coating, although the oxide layer is partially absorbed by the molten glass.

The bond strength of individual glass-metal specimens can be estimated by observation of the Cr and Co compositional profiles after AES analysis. Specimens with high bond strength typically fracture between the metal and metal oxide layer. Specimens with thicker than optimum oxide layers generally have poor bond strength, with fracture

occurring within the oxide layer. Low bond strength is also observed for coated specimens with oxide layers which are too thin to maintain good chemical bonding during the coating operation. Even an oxide layer which is of the proper thickness for optimal glass-metal bonding is not protective during prolonged heating, however, as bond strength generally decreases with continued thermal treatment. During a prolonged heat treatment, such as during a crystallization cycle, a more protective oxide layer is needed to prevent excessive diffusion of metal ions into the glass. This continued diffusion decreases glass-metal adherence by causing either a loss of saturation of the metal oxide in the glass or the formation of voids at the glass-metal interface.

The Suitability of the Immersion Process for Coating Vitallium Implants with Bioglass

As discussed in Chapter II, the immersion coating process is a method of choice for coating Vitallium with Bioglass because:

1) the short time at coating temperature (e.g., 3 sec.) does not significantly decrease the mechanical properties of the Vitallium substrate (as in the frit enameling method), and 2) a smooth, thick coating of glass can be obtained without the excessive porosity and corrosion which has been encountered in using the flame spray technique. One of the disadvantages of the immersion technique is the difficulty in the coating of complex shapes, as the molten glass is too viscous at the coating temperature to penetrate into internal cavities during the short immersion time. The coating of these types

of parts could be more easily accomplished by dipping the substrate into a Bioglass frit solution and then firing the frit layer to form a smooth glass coating.

A secondary objective of this investigation has been to produce a Bioglass-Vitallium composite with increased coating adherence. The strength of the Bioglass-Vitallium bond is a major factor in the proper functioning of the device during use as an implant. One of the potential medical uses of Bioglass-coated-Vitallium is in total hip replacements. In this application, the Bioglass coated shaft of the implant is placed inside the femur with the uncoated head of the implant in position at the hip joint. Failure of the Bioglass-metal bond may result in loosening of the implant and further surgery may be necessary to remove the device.

The glass-metal bond strength of a Bioglass-Vitallium hip prosthesis required to insure the integrity of the device is not known at this time. Various investigators have sought to determine the load placed on a femur during normal movement. Rydell⁹⁴ found that standing on one leg creates a force of the hip joint which is $2\frac{1}{2}$ times the body weight, and running causes forces equal to 5 times body weight. He estimates that 12 to 15 times body weight can be tolerated by the hip joint before fracture. Fessler⁹⁵ found that the angle and force along the femur change with the tilt angle of the pelvis. The angle of the joint force is not constant; it increases as the force increases so that greater forces act along the neck of the femur where the bone is able to support them. This change in angle with an increase in

force means that more of the force would be distributed along the femur and not concentrated at the implant site. However, some bending force would remain on the implant, and a rotation of the hip would cause the coating on the implant to be stressed in torsion.

The high modulus of the Vitallium substrate would keep the Bioglass coating (which is under a slight compression) from fracturing under normal bending loads. It is not known what portion of an applied load would act to cause shearing of the glass coating from the metal, but in normal loading it would be only a small fraction of the total load. A twisting motion of the implant in the femur would be more likely to concentrate stress at the interface of the coating and substrate, and thus torsion may well be the most severe type of loading encountered by a coated implant.

Based on the average shear strength of Bioglass-Vitallium specimens coated by the optimized immersion process, a 5-inch Bioglass-coated section of a $\frac{1}{2}$ inch diameter implant shaft could withstand a load of 3560 Kg without failure of the coating. The preliminary fatigue results indicate that a load (acting totally in shear) of more than 300 Kg could be sustained by this implant indefinitely (i.e., more than 2 million cycles) without failure at the Bioglass-Vitallium interface.

In evaluating the suitability of Bioglass-Vitallium devices for use in dentistry, it was determined that the average shear strength of the glass-metal interface is similar in value to the estimated stress on a mandibular molar during mastication (70 Kg/cm^2). Based

on this finding, it is recommended that the use of Bioglass-coated-Vitallium be restricted to anterior teeth or implants which do not receive the full stress during mastication. This is similar to the restriction placed on dental porcelain-fused-to-metal crowns, as they are rarely used for posterior teeth where they would be subjected to full biting loads.

The immersion process has been shown to be a satisfactory method for coating Bioglass-to-Vitallium based on both the strong coating adherence and the fact that the corrosion resistance and the mechanical properties of the Vitallium are not reduced by the coating process. Good corrosion resistance is important for an implant, as metallic corrosion products in the surrounding tissue have been shown to cause infection and tissue necrosis in some cases. There was some concern in the initial stages of the coating program that the dark, narrow (1 mm) band at the glass-metal junction of specimens tested in vivo was due to corrosion resulting from the use of the immersion techniques. However, as this dark area was observed on specimens immediately after coating, it was determined that it was the result of heavy oxidation due to near contact with the molten glass at 1350°C.

Vitallium has excellent corrosion resistance in most environments and does not become sensitized during the coating operation. By comparison, normal grades of stainless steel are subject to sensitization, so those alloys which are to be welded or used at high temperatures generally contain very low carbon (e.g., less than 0.01%) so that the corrosion resistance is retained after heating. Vitallium has

high carbon (0.25%) but the Mo in the alloy ties up most of the free carbon so that it is not available to react with chromium (and thus reduce the corrosion resistance).

Localized corrosion at the Bioglass-Vitallium junction may occur because of the depletion of the surface layer of chromium during oxidation to Cr_2O_3 . The glass absorbs part of the chromium-rich oxide during immersion, leaving a small zone which is more subject to corrosion than the bulk alloy. Also, partial fracturing of the coating (in solution) would expose the underlying metal surface (which is depleted in Cr) to the corrosive effects of the solution. Examination of the glass-metal junction of each specimen tested in vitro or in vivo, however, showed that no corrosion was evident in any case.

In summary, the immersion method is a satisfactory means of coating Bioglass-to-Vitallium; good coating adherence is obtained with the use of an optimized immersion process, and the Vitallium substrate retains its high mechanical properties and excellent corrosion resistance through the coating and annealing operations.

Conclusions

1. Oxidation of the Co-Cr-Mo alloy in either air or a partial vacuum produces a high-Cr oxide layer and a Cr-depleted zone next to the bulk metal. The oxygen pressure during heating affects only the depth of oxidation and not the relative profile of the elements.
2. Only a thin oxide layer ($\sim 0.3 \mu\text{m}$) is required for maximum bond strength between the Co-Cr substrate and the silicate glass

coating applied by the immersion process. Oxide layers thicker than $0.4\text{ }\mu\text{m}$ are generally weaker and failure occurs predominately within the oxide itself (as indicated by the high Cr on both the metal and glass fracture surfaces). Thin oxide layers ($<0.2\text{ }\mu\text{m}$) tend to be discontinuous (patches of Cr_2O_3) and low glass-metal adherence is typically observed. Specimens with high bond strength generally fracture in areas of low Cr in the metal and high Cr in the glass -- indicating that for optimum bonding most of the oxide layer must be dissolved in the glass.

3. The metal oxide layer profile is retained in the glass layer (at the interface) during the immersion coating process as diffusion times is limited. A peak of Cr generally occurs about $0.1\text{--}0.2\text{ }\mu\text{m}$ into the glass with only limited diffusion of Co, Mo, Si, Ca, Na and P occurring across the interface. Part of the oxide layer may be "floated off" the surface of the metal as it is absorbed by the molten glass.
4. With short heating times Cr is the predominate metallic element in the glass; during prolonged heat treatment the relative amount of Co increases as Co diffuses much further into the glass than Cr. Cr tends to concentrate near the interface, due perhaps to its reaction with P_2O_3 .
5. Continued heat treatment of the glass-metal composite at a sufficiently high temperature (800°C or greater) causes a loss of bond strength. The thin, partially dissolved Cr_2O_3 layer on the metal substrate is not protective enough to prevent the

diffusion of metal ions into the glass phase. The decrease in metal saturation in the glass at the interface and the formation of voids at the glass-metal interface (by the continued diffusion of metal ions) are two possible explanations for the lower bond strength observed for heat treated specimens.

6. Good adherence of the glass coating is dependent on the control of conditions which establish a high degree of chemical bonding. Increasing the degree of mechanical interlocking by roughening the surface of the metal substrate is of secondary importance when compared to such factors as the maintenance of metal oxide saturation in the glass interfacial layer.
7. The fatigue strength of the Bioglass-Vitallium bond is relatively low due in part to the presence of porosity at the glass-metal interface. Metal cleaning and degassing techniques are relatively ineffective for this particular alloy, and a change to an alloy with a lower carbon content is desirable if higher bond strength is required.
8. The push thru shear test is an acceptable method for measuring immersion-coated glass-metal specimens, but the results are sensitive to surface cracks produced during specimen preparation. Also, tests of this nature are somewhat subject to the amount of radial "gripping" force caused by a difference in the thermal expansion coefficients between glass and metal.
9. The immersion process is a satisfactory method for producing Bioglass-coated-Vitallium implants, as the reactivity of the

Bioglass is not affected by the coating operation and there is no incidence of increased corrosion at the glass metal junction due to metal sensitization.

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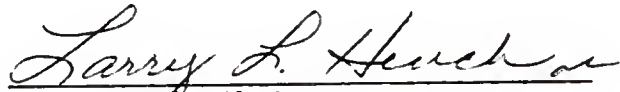
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BIOGRAPHICAL SKETCH

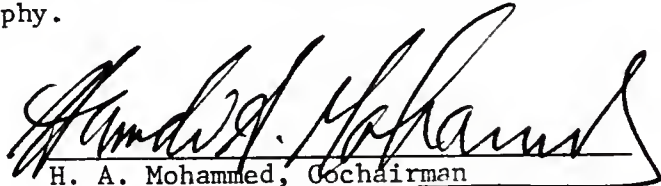
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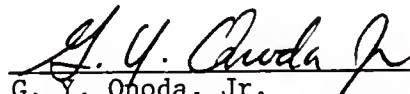
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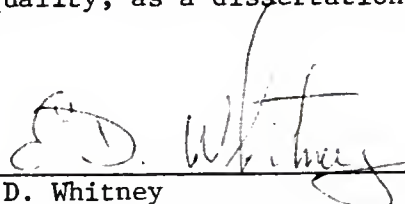
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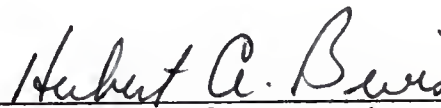
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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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